Thermoelectric Thermometry

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LEEDS & NORTHRUP COMPANY, PHILADELPHIA, PA.

Errata

Page	14	Third line from bottom, 0.1258" should be 0.1285"
"	18	Second paragraph, line 2, the organization referred to should be Scientific Apparatus Makers Association.
"	35	In Fig. 18, "Nv" should be Mv
"	42	In Fig. 20, "Key K-1" should be Key K_1 " " " "Key K-2" " " Key K_2
"	43	Second paragraph, line 6, "Key K" should be Key K_1
"	44	Second paragraph, line 1, "Key K" should be Key K_1
"	54 & 56	Figs. 28 and 29 are transposed
"	82	Ninth Col., line 7 from bottom, "445" should be 545

Thermoelectric Thermometry

a monograph *on the materials*
and methods involved
in the measurement
of temperature
with the aid of thermocouples
in accordance with
the practice of
the Leeds & Northrup Company

written by **P. H. Dike,** *Ph.D.*
September, 1954

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Paul H. Dike

Philadelphia, September 1954

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chapter 1

Elementary principles of temperature measurement by thermoelectric methods

A. Seebeck Effect

It was discovered by T. J. Seebeck* that if a circuit is formed consisting of two dissimilar metallic conductors A and B, and if one of the junctions of A and B is at a temperature T_1 while the other junction is at a higher temperature, T_2, a current will flow in the circuit. A current continues to flow as long as the two junctions are at differing temperatures. The emf producing this current is called the Seebeck thermal emf. Conductor A is said to be positive with respect to B if the current flows from A to B at the cooler of the two junctions.

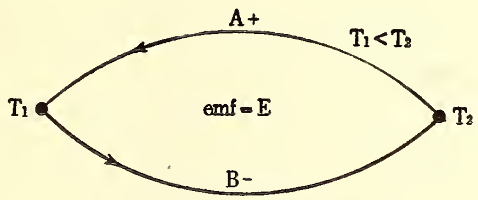


Fig. 1 Seebeck Effect

B. Peltier Effect

Peltier** found that when a current flows across the junction of two metals it gives rise to an absorption or liberation of heat. If it flows across the junction in one direction heat is absorbed, while if it flows in the other direction heat is liberated. If the current flows in the same direction as the current produced by the Seebeck effect at the hot junction in a thermoelectric circuit of two metals heat is absorbed while at the cold junction heat is liberated. Thus, for example, heat is absorbed when a current flows across an iron-constantan junction from the constantan to the iron, iron being thermoelectrically positive with respect to constantan. The heat liberated or absorbed is proportional to the quantity of electricity which crosses the

* *Abt. d. Konigl, Akak. d Wiss Berlin 1822-23, p. 265, Evidence of the thermal current of the combination Bi-Cu by its action on magnetic needle.*

** *Peltier M. Ann. Chim, phys. 56, p. 371, 1834, Investigation of the heat developed by electric currents in homogeneous materials and at the junction of two different conductors.*

junction. The amount of heat liberated or absorbed when one coulomb of electricity crosses the junction is called the Peltier effect at the temperature of the junction. Expressing the heat in joules it can be shown that the magnitude of the Peltier effect is given by the product of the absolute temperature of the junction into the rate of change of the thermal emf of the junction at that temperature.

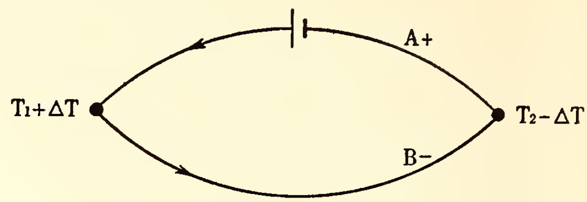


Fig. 2 Peltier Effect

For example we may consider the case of an iron-constantan thermocouple with its cold junction in melting ice and its hot junction at 227 C (500 absolute). From the temperature-emf table for iron-constantan we find that the thermal emf of such a thermocouple changes at the rate of 55 microvolts per degree C at 500 K. Then the magnitude of the Peltier effect is given by $500 \times 55 \times 10^{-6} = 0.0275$ joule per coulomb.

To compute the cooling effect on the hot junction produced by the thermoelectric current we may take the case in which the emf is being measured by means of a millivoltmeter, and the total circuit resistance is 100 ohms. With the cold junction at 0 and the hot junction at 227 C the emf is 0.0125 volt. The current is therefore:

$$I = \frac{E}{R} = \frac{0.0125}{100} = 0.000125 \text{ ampere.}$$

Since coulombs = current in amperes $\times$ time in seconds, time in seconds for one coulomb to pass $= \frac{1}{0.000125} = 8000$ sec. One coulomb absorbs 0.0275 joule = 0.0066 calorie. Therefore heat is absorbed at the rate of $\frac{0.0066}{8000} = 8 \times 10^{-7}$ cal/sec. If we assume further that the iron and constantan wires are so thin that the heat capacity of their junction is only 0.001 calorie, and that there is no flow of heat to the junction from the wires or their surroundings, it will require $0.001 \times 8 \times 10^{7} = 80000$ seconds (22 hours) to reduce its temperature from 227 to 226 C. Obviously the Peltier effect produces no measurable change in the temperature of the junction when the only current across it is that due to the thermal emf.

C. Thomson Effect

On the basis of thermodynamic reasoning, treating the Seebeck circuit as a reversible heat engine, it can be shown that if the only reversible thermal effects in the circuit are the Peltier effects at the junctions, the emf around a circuit whose cold junction is kept at a constant temperature should be proportional to the difference between the temperatures of the hot and cold

junctions. This is contrary to experience. For example, in a circuit made up of iron and copper wires, with the cold junction in melting ice, the emf increases as the temperature of the hot junction is increased, but more and more slowly, until a maximum is reached. The emf decreases with further rise in temperature, passes through zero and reverses in sign.

These phenomena led Lord Kelvin (Sir William Thomson) to look for reversible heat effects when an electric current flows through a conductor in which there is a temperature gradient. He found that when a current flows along a copper wire whose temperature varies from point to point, heat is liberated at any point P where the current at P flows in the direction of the flow of heat at P; i.e., when the current is flowing from hot places to cold, while heat is absorbed at P when the current flows in the opposite direction. In iron, on the other hand, heat is absorbed at P when the current flows in the direction of the flow of heat at P, while heat is liberated when the current flows in the opposite direction. In the copper wire the current tends to diminish the differences in temperatures, while in the iron wire it tends to increase them. This effect produced by a current flowing along a conductor in which there is a temperature gradient is called the Thomson effect.***

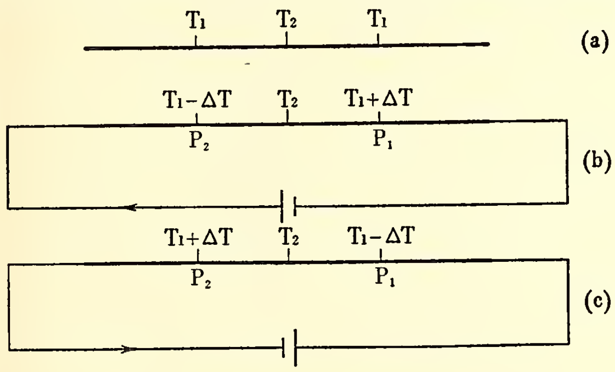


Fig. 3 Thomson Effect

Fig. 3 (a), (b) and (c), represents a bar of metal which is heated at its mid-point to a temperature T_2. A current from an external source is passed through it. Points P_1 and P_2 which were at equal temperature T_1 lower than T_2, when no current was flowing have their temperatures changed to $T_1 + \triangle T$ and $T_1 - \triangle T$ respectively when the current flows in one direction, and to $T_1 - \triangle T$ and $T_1 + \triangle T$ when the current is reversed. The case shown corresponds to the behavior of copper.

Like the Peltier effect, this is a reversible heat effect, unrelated to the irreversible Joule heating which is proportional to the square of the current. It is distinguished from the Peltier effect, in that it occurs in a homogeneous conductor rather than at the junction of two dissimilar conductors.

The Thomson effect has still less influence on the temperature of the conductor than the Peltier effect has on that of the junction. It can be detected experimentally only by the use of large currents and sensitive devices for measuring differences in temperature.

****Thomson, W. Trans. Edinb. Soc. 21, p. 153, 1847, Theory of thermoelectricity, etc. in crystals. Also Math. Phys. Papers, 1, pp. 232 and 266, 1882.*

The emf observed by Seebeck and which is the basis of thermoelectric thermometry, is the algebraic sum of the Peltier emf at the junctions and the two Thomson emf's in the two dissimilar wires. Instead of the simple relationship, $E = aT$, where E is the observed emf when there is a difference of temperature of T degrees between the cold and the hot junctions, and a is a constant, it is found that E is more nearly represented by the relationship $E = aT + bT^2$. This latter expression is only approximate. Secondary effects such as changes in grain structure with changing temperature introduce considerable departures from this parabolic relationship between E and T in the case of many combinations of conductors.

D. *Thermoelectric Laws*

While the theory of the thermoelectric circuit can be worked out on thermodynamic principles, and while the phenomena involved can be qualitatively deduced from the electron theory of metals, there is as yet no way of predicting the thermoelectric characteristics of a metal or an alloy from its structure or its composition. The thermal emf to be expected from a given pair of elements for a certain temperature difference cannot be predicted with any degree of confidence on a theoretical basis. The temperature-emf curves for thermocouples are purely empirical, having no precise theoretical derivation. They are based on interpolations between measured values at certain known temperatures.

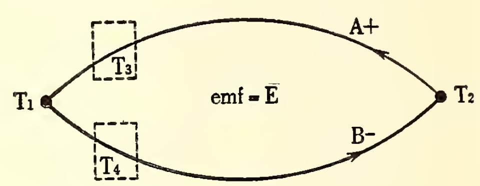


Fig. 4 E Unaffected by T_3 and T_4

Thermoelectric circuits are subject to certain definite laws. One of these (Fig. 4) is that an electric current cannot be maintained in a circuit of a single homogeneous metal by the application of heat alone. A consequence of this law is that if one junction of two dissimilar homogeneous metals is maintained at a temperature T_1 and the other junction at a temperature T_2, the thermal emf developed is independent of the temperature gradient and distribution along the wires.

A second law (Fig. 5) indicates that if in a circuit consisting of two homogeneous metals A and B with their junctions at temperature T_1 and T_2 a third metal C is introduced by cutting A, forming two junctions of A and C, and if the temperature of C is uniform over its whole length, the total emf in the circuit will be unaffected. This is the law of intermediate metals in one of its various forms. Combining this statement with the law first given it will be seen that if A and B are separated at the junction at temperature T_1 and two junctions AC and CB are formed at temperature T_1 while C may extend into a region of very different temperature; e.g., T_3, the emf

in the circuit will be unchanged. That is, $E_{AC} + E_{BC} = E_{AB}$. From this it follows (Fig. 6) that if the thermal emfs of any two metals with respect to a reference metal such as C is known, then the emf of the combination of the two metals is the algebraic sum of their emf's against the reference metal.

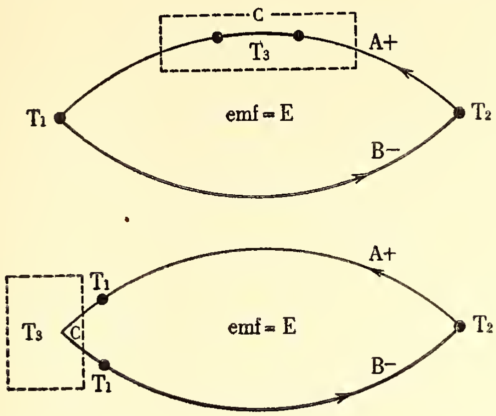


Fig. 5 E Unaffected by Third Material C

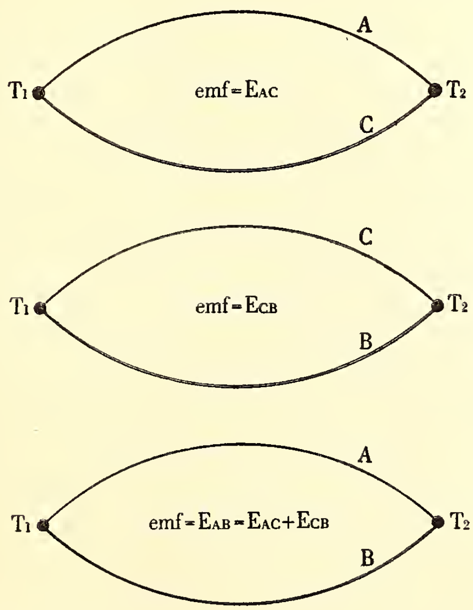


Fig. 6 EMF'S are Additive for Materials

A third law (Fig. 7) states that if a pair of metals produces a thermal emf E_1, when its junctions are at temperatures T_1 and T_2 and a thermal emf of E_2 when its junctions are at T_2 and T_3, the emf generated when the junctions are at T_1 and T_3 will be $E_1 + E_2$.

In general, it may be stated that the algebraic sum of the thermoelectric emf's generated in any given circuit containing any number of dissimilar

homogeneous metals is a function only of the temperatures of the junctions. If all but one of the junctions in such a circuit are maintained at some reference temperature, the emf generated depends only on the temperature of that one junction and can be used as a measure of its temperature.

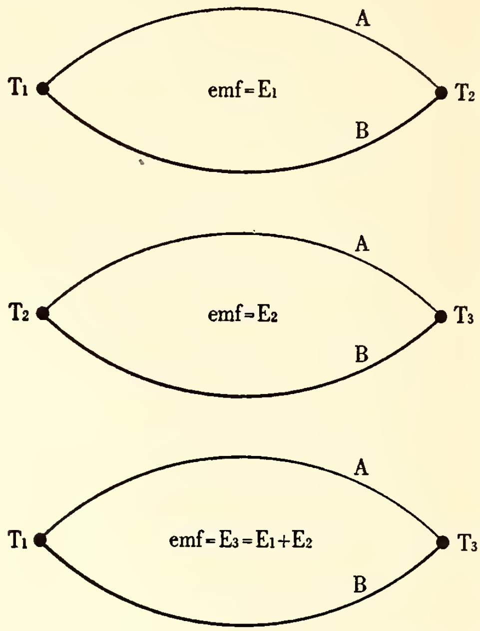


Fig. 7 EMF'S are Additive for Temperature Intervals

E. *Thermometry by Thermoelectric Means*

Experience has shown that there is a definite reproducible relationship between the difference of temperature of the junctions of a thermoelectric circuit and the emf in the circuit. Since this emf is readily measured by measuring the current produced in a circuit of fixed and known resistance or by balancing it against an equal and opposite emf by means of a potentiometer, it provides a means for the measurement of temperature differences. If the temperature of one of the junctions is at some known temperature, T_o, such as that of melting ice, the measurement of emf, and hence of $\triangle$ T ($= T_x - T_o$) makes it possible to determine the temperature of the other junction by algebraic addition of $\triangle$ T and T_o. ($T_x = T_o + \triangle T$). The thermocouple with its emf-measuring device becomes a thermometer or a pyrometer. As such, with proper choice of thermoelectric materials, the method can be used for measuring temperatures from close to absolute zero to temperatures considerably above 1700 C (3000 F).

Essentially, a thermoelectric thermometer consists of two wires, A and B, welded together to form the "hot" or *measuring junction,* and of a device for measuring emf connected to the free ends of A and B. The junctions of A and B with this device constitute the *reference junction* and are held at a definite temperature T_1. For laboratory purposes, T_1 is usually the melting point of ice and the reference junctions are immersed in an ice bath. The

introduction of the metal C of the measuring device has no effect on the emf in the circuit so long as its junctions with A and B are both at temperature T_1. The emf is dependent only on $T_2 - T_1$, and the relationship between emf and temperature difference having once been determined for the combination of A and B at suitably distributed known values of T_2, temperatures can be deduced from measured emfs.

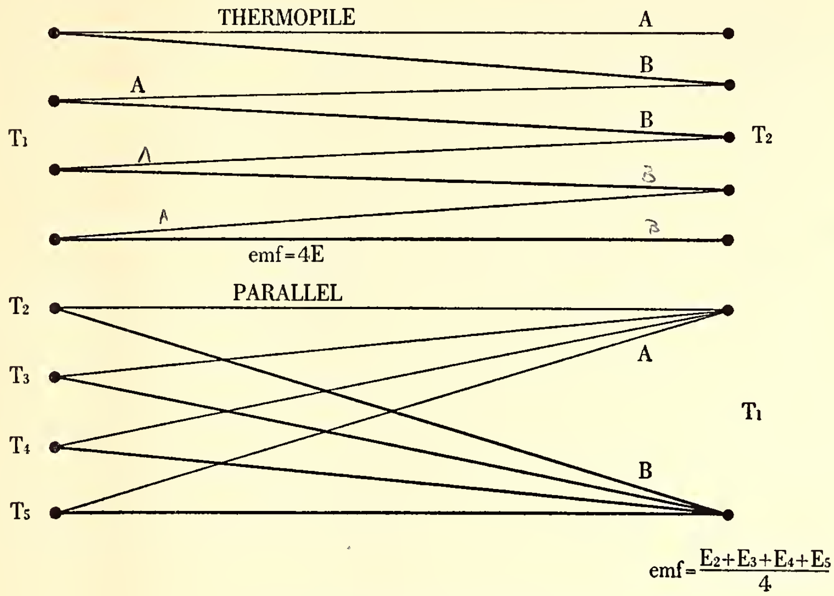


Fig. 8 Multiple thermocouples

The two wires, A and B, with their welded measuring junction constitute a *thermocouple.* A number of similar thermocouples may be connected in series with all the measuring junctions at temperature T_2 and the reference junctions at T_1. Such a series is called a *thermopile,* and, with n thermocouples in series generates an emf n times as great as a single thermocouple. If n thermocouples are connected in parallel, the emf generated is the same as for a single thermocouple. If all the thermocouples are of equal resistance and their measuring junctions are at various temperatures T_2, T_3........ T_{n+1} the emf generated will correspond to the mean of the temperatures of the individual junctions.

chapter 2

Thermocouple materials

A. General

Of the vast number of possible combinations of metals, alloys and nonmetallic conductors only a few are in actual use in thermoelectric thermometry. These few have been chosen from the many on the basis of their thermoelectric powers, their stability and reproducibility, their melting points, mechanical properties and cost.

The various conductors can be tabulated in an order such that, at some specified temperature, each item in the list is thermoelectrically negative with respect to all those above it and positive with respect to all those below it. The tabulation resembles the arrangement of metals in the electrochemical electromotive force series, but the position of a metal in one tabulation has no relation to its position in the other. The order may vary somewhat with the temperature at which the emf is observed:

Thermoelectric Series for Selected Metals and Alloys

100°C	500°C	900°C
Antimony	*Chromel*	*Chromel*
Chromel	*Nichrome*	*Nichrome*
Iron	*Copper*	*Silver*
Nichrome	*Silver*	*Gold*
Copper	*Gold*	*Iron*
Silver	*Iron*	$Pt_{90}Rh_{10}$
$Pt_{90}Rh_{10}$	$Pt_{90}Rh_{10}$	*Platinum*
Platinum	*Platinum*	*Cobalt*
Palladium	*Cobalt*	*Alumel*
Cobalt	*Palladium*	*Nickel*
Alumel	*Alumel*	*Palladium*
Nickel	*Nickel*	*Constantan (Adams)*
Constantan (Adams)	*Constantan (Adams)*	
Copel	*Copel*	
Bismuth		

To form a sensitive thermocouple, a pair of materials should be well separated in the list. The materials chosen should have melting points higher than the highest temperature at which they are to be used. They should resist corrosion in the medium and at the temperature to which they are to be exposed. They should be homogeneous, should not have too high an electrical resistance, etc. Each added restriction narrows the choice until only

a few are left. Of these the majority may be eliminated by considerations of economics of procurement which weigh heavily in the final choice for industrial applications.

B. Thermoelectric Power

The thermoelectric properties of materials are compared by measuring the emf's produced when a junction of the given material with some standard material is held at various known temperatures while the "reference" junction is held at 0 C. Thomson, in his work on thermoelectricity used lead as the reference material, primarily because its "Thomson emf" is very small. Platinum is now used for this purpose because of its stability, its availability in a very pure state, and its high melting point. It has an appreciable Thomson emf.

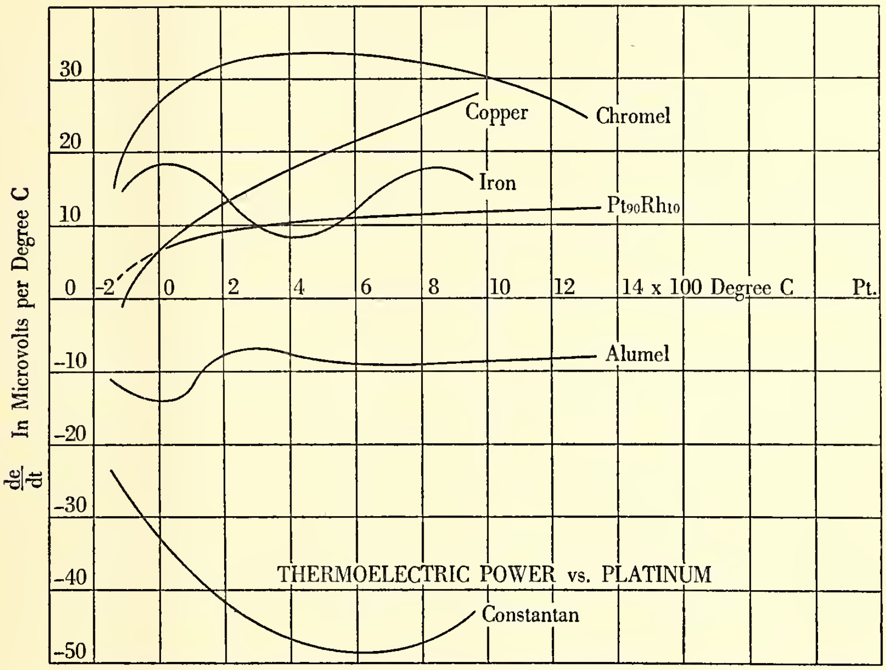


Fig. 9 Thermoelectric Powers of Common Thermocouple Elements Against Platinum

Thermoelectric relationships are most conveniently represented by graphs or tables in which thermal emf's against platinum, with the reference junction held at 0 C, are shown as a function of the temperature of the measuring junction. The relationship is rarely found to be a linear one, since for linearity it would be necessary that the Thomson emf in the material in question should be equal to that in platinum, at all temperatures. To a rough approximation the temperature-emf curve usually has a parabolic form. Its equation is of the form

$$e = aT + bT^2$$

where e is the emf when the reference junction is at 0 C, and the measuring junction at a temperature T, and a and b are constants.

$$\frac{de}{dT} = a + 2bT$$

$\frac{de}{dT}$ is the change in emf per degree change in T at the given temperature. It is called the *thermoelectric power* of the thermocouple. If the temperature-emf curve were strictly parabolic the thermoelectric power would be a linear function of T and a plot of $\frac{de}{dT}$ against T would be a straight line. In the case of pure copper this condition is nearly satisfied in the range from 100 to 500 C, but is departed from widely below 0 C. The alloy of platinum with 10 per cent rhodium gives a thermoelectric power curve which is nearly linear from 400 to 1100 C. The impure metals and the alloys used in commercial thermocouples have very non-linear thermoelectric power vs. temperature curves. See Fig. 9.

The approximate emf that will be generated by a thermocouple made up of any two of the metals, the thermoelectric power – temperature curves of which are known, can be computed, by mechanical integration. Assuming that the reference and the measuring junctions are at T_1 and T_2 respectively, the emf generated is given by the area bounded by the curves for the two metals, and the ordinates at T_1 and T_2. If the thermoelectric power is expressed in microvolts per degree C the emf will be given in microvolts for the given difference of temperature.

The values arrived at by this method are not precise, but serve to predict orders of magnitude of emf to be expected from untried combinations.

C. *Antimony-Bismuth*

The classical combination of thermoelectric materials is that of antimony and bismuth which occupy positions near the top and the bottom respectively of the thermoelectric series. It is a combination which was much used for thermopiles in the study of radiation laws and in attempts to produce thermoelectric batteries for the direct transformation of heat energy into electrical energy. The thermoelectric power of antimony against bismuth at room temperature is about 122 microvolts per degree C. Both metals are difficult to draw into wires. Antimony melts at 630 C (1166 F) and bismuth at 271 C (520 F). Both have high electrical resistivities. Consequently, this combination is not attractive as a practical thermocouple. Seebeck's original discovery of the thermoelectric emf was based on a thermocouple made up of antimony and copper.

D. *Platinum-Platinum + 10% Rhodium*

1. General

This thermocouple, often called the Le Chatelier thermocouple, is, from the scientific standpoint, the most important of the thermocouples now in use. It is used for defining the International Temperature Scale from 630.5 C (the freezing point of antimony) to 1063 C (the gold point); for precise temperature measurements between 0 and 1500 C; and for temperature measurements where its chemical inertness and its stability at high temperatures in oxidizing atmospheres make its choice in preference to base metal

couples imperative. It is not used for sub-zero temperatures since its thermoelectric power becomes too low for accurate measurements and becomes zero at about −138 C. Its two elements fall close together in the thermoelectric series, its thermoelectric power being about 6 μv/deg. C between 0 and 100 C, but its advantages outweigh its relatively low sensitivity, which is not a serious drawback with modern instrumentation.

The choice of platinum as a thermoelectric material was based not only on its thermoelectric properties but also on its excellent mechanical and chemical properties, its fairly low electrical resistivity, and its homogeneity when properly heat treated. This latter property results in freedom from the parasitic thermal emf's sometimes called the Becquerel effect. To secure a companion for platinum which would also have its advantageous properties, it was necessary to choose an alloy of platinum with another noble metal of the platinum group. The only practical metals were iridium and rhodium. An alloy of $Pt_{90}Ir_{10}$ gives a considerably higher thermoelectric power against Pt than $Pt_{90}Rh_{10}$, but its physical properties are not as good, since it becomes brittle at high temperatures and there is a greater tendency for the iridium than for the rhodium to evaporate from the alloy at high temperatures. It forms a less stable thermocouple than the alloy of platinum with rhodium. Other noble metal alloys have been tried, such as $Pt_{92}Re_{8}$, which has a thermoelectric power against platinum almost three times as great as $Pt_{90}Rh_{10}$, but which is much less stable.

The alloy $Pt_{87}Rh_{13}$ is used to some extent in place of $Pt_{90}Rh_{10}$, in industrial applications. It was introduced when it was found that instrument scales calibrated to correspond to somewhat impure platinum were in error when purer platinum became available, which gave a lower emf. The substitution of $Pt_{87}Rh_{13}$ for $Pt_{90}Rh_{10}$ compensated for the change and made the existing instruments read correctly. The expedient has become self-perpetuating in a small group of pyrometers in spite of the fact that rhodium is about ten times more costly than platinum, resulting in a higher price for the alloy more rich in rhodium.

The most outstanding fault of the Pt-$Pt_{90}Rh_{10}$ thermocouple is its rapid deterioration in reducing atmospheres at elevated temperatures which results from gas absorption in the metals and from the reduction of metallic oxides in the protecting tube and the absorption of the reduced metals by the platinum, tending to change the emf. This is a common fault of most thermocouple materials at temperatures above 1000 C.

In oxidizing atmospheres at temperatures from 1100 C upward, there is said to be a tendency for rhodium to volatilize more rapidly than platinum, gradually decreasing the percentage of rhodium in the alloy and thus decreasing the emf. If the volatilized rhodium can deposit on the platinum wire, it alloys with it and further decreases the emf. This latter effect can be avoided by enclosing the wires in a continuous double-bore ceramic insulator, so that the rhodium vapor cannot reach the platinum.

In service the platinum wire is subject to grain growth, which eventually causes the wire to consist of a series of crystals each occupying its entire cross-section. This has little effect on the emf of the thermocouple, but contamination and volatilization proceed more rapidly and the wire becomes

brittle, resulting eventually in failure. Thermocouples left permanently in a fixed position last longer than those subject to mechanical disturbance.

2. Pt—$Pt_{90}Rh_{10}$ Thermocouple as a Temperature Standard

The International Temperature Scale, adopted by the Seventh General Conference of Weights and Measures in 1927, and reaffirmed in 1948 with slight change, makes use of the Pt-$Pt_{90}Rh_{10}$ thermocouple to interpolate temperatures between 630.5 C and 1063 C. If the reference junction is kept at 0 C, the emf generated when the measuring junction is at a temperature t C between 630.5 and 1063 C, is given by the formula

$$e = a + bt + ct^2$$

The constants a, b, and c, are determined by calibration at the freezing points of antimony, of silver and of gold, and values for e are computed for temperatures within the specified range, constituting a calibration table. Representative values for these constants as determined at N.B.S. for two thermocouples are as follows, where e is expressed in microvolts:

	a	b	c
Thermocouple 1	–328.86	+8.29990	+0.00161064
Thermocouple 2	–353.18	+8.35865	+0.0015745

A thermocouple thus calibrated is used as a reference standard of temperature within the range specified just as the calibrated platinum resistance thermometer is standard below 630.5 C and the optical pyrometer is standard above 1063 C. The useful range of the platinum thermocouple is not restricted to the temperatures which it serves to define, though the formula determined for it holds exactly only within this range.

3. Working Standard Platinum Thermocouple

For use as a working standard of temperature in the laboratory where it is desirable to be able to measure temperatures outside the above specified range without changing the method of measurement, the platinum thermocouple is a very useful tool. It may be used in the range from 0 up to 1500 C and, with special precautions and for short periods even up to 1650 C. To be used for this purpose, the thermocouple for which the a, b, and c values have been determined should be calibrated at several fixed points below 630.5 C, which may be selected from the list of fixed points given on page 60. If more convenient it may be calibrated against a certified platinum resistance thermometer at properly distributed temperatures below the antimony point. A smooth curve is drawn through these points on the temperature-emf chart as well as through the silver and gold points, already determined. Departures of this curve between 630.5 and 1063 C from the curve computed from the values of a, b, and c by substitution in the formula are noted and adjustments are made in the experimental curve to make it fit the computed curve more closely. The corrected curve is then extrapolated to temperatures above 1063 C. This extrapolation may be checked with the aid of an optical pyrometer. It should be emphasized that the constants a, b, and c are to be used only in the range from 630.5 to 1063 C.

The working standard platinum thermocouple is much used for the calibration of base-metal thermocouples as well as for many other precise temperature measurements, where its stability is a valuable asset.

4. Industrial Platinum Thermocouples

The platinum thermocouple is used in industry for measuring temperatures which are too high for resistance thermometers or for base-metal thermocouples, and where radiation or optical pyrometers are not satisfactory. If the temperature is to be recorded or automatically controlled, optical pyrometers cannot be used. The radiation pyrometer may not be able to sight satisfactorily on the body, the temperature of which is required. In these cases, the platinum thermocouple is often the only practical means of temperature measurement. A standard temperature-emf table has been adopted for platinum thermocouples based on the calibration of a considerable number of representative couples from various sources. Any $Pt\text{-}Pt_{90}Rh_{10}$ thermocouple from a reputable source can be assumed to match this table to ± 0.25 per cent of the measured emf. The difference curve for the deviation of any given thermocouple from the tabular values is practically a straight line, so that a one-point check at a suitable temperature is adequate to test the calibration of a particular thermocouple. If a platinum thermocouple has been used for measuring a temperature as high as 1600 C it should not be used later at lower temperatures without making a one-point check for change in calibration. After any possible exposure at high temperature to a reducing atmosphere, even in a glazed porcelain protecting tube, the platinum thermocouple should be checked and if necessary reconditioned by suitable processes. (See p. 21)

*E. Chromel-Alumel Thermocouples**

1. Chromel

Chromel P is an alloy having the composition $Ni_{90}Cr_{10}$. Its thermoelectric power against platinum is higher than that of any other readily available alloy, reaching a maximum of about 35 μv per degree C at 400 C (750 F), and decreasing to about 25 μv at 50 C (120 F) and at 1300 C (2400 F). Like other nickel-chromium alloys it is resistant to oxidation at high temperatures.

2. Alumel

Alumel is an alloy which was developed by the Hoskins Mfg. Co. with the express purpose of serving as the negative element to accompany Chromel. Nickel would have been used, except for the molecular rearrangement which occurs between 230 and 390 C which makes it unsuited for thermoelectric work over this range. An alloy of pure nickel and aluminum stands up well at high temperatures, but becomes brittle at low temperatures. An alloy having the composition $Ni_{94}Mn_3Al_2Si_1$ was found to have good characteristics up to temperatures of the order of 1300 C. This alloy was named "Alumel". Its thermoelectric power is from -7 to -9 μv per degree C from 200 to 1300 C (400 to 2400 F).

3. Characteristics

The thermoelectric power of the couple is fairly constant; about 40 μv over the range from 250 to 1000 C and even up to 1300 C it does not drop below 35 μv/deg. C. As a result the temperature-emf curve for the thermocouple is fairly linear, and its emf's are more than four times greater than those of the platinum couple at corresponding temperatures. At temperatures below

** The words Chromel and Alumel are trade names of Hoskins Manufacturing Co.*

500 C this greater sensitivity is often advantageous. The oxidation-resistant characteristics of the Chromel-Alumel thermocouple are better than those of other base metal thermocouples in general use, and permit its continuous use at temperatures up to 1200 C without rapid deterioration, and for limited times as high as 1300 C. It is subject to the same limitation as to reducing atmospheres as the platinum thermocouple at those high temperatures, and is recommended for use only in oxidizing atmospheres.

4. Limits of Error

Since Chromel and Alumel wires are produced by a single manufacturer, who aims to keep the materials uniform within narrow limits, it has been possible for N.B.S. to publish standard tables for Chromel-Alumel thermocouples*, which give the temperatures corresponding to given emfs with limits of error as set by the manufacturer of ± 5 F (2.8 C) in the range 32 to 660 F (0-350 C) and $\pm \frac{3}{4}$ per cent between 660 and 2300 F (350-1260 C). These limits are for thermocouples made up by random selection from stock wire.

The manufacturer's announced policy is to produce wires which give an emf of 36.20 mv, when one junction is at 32 F and the other at 1600 F. In practice, most of the Chromel wire produced gives 28.50 ± 0.10 mv. against platinum when one junction is at 32 F and the other at 1600 F. Most of the Alumel wire gives -7.70 ± 0.10 mv. against platinum under the same conditions. The completed couple should therefore give 36.20 ± 0.20 mv. with one junction at 32 F and the other at 1600 F. It was formerly the practice to utilize Chromel and Alumel whose characteristics fall outside the above specifications by combining a Chromel whose emf against platinum is too low with an Alumel which is high, or vice versa. Improvements in the control of the production of these alloys has allowed this procedure to be discontinued.

5. Applications

While the Chromel-Alumel thermocouple was developed for pyrometric purposes it may also be used for measuring sub-zero temperatures, having a useful range starting as low as –200 C. At –200 C its thermoelectric power is about 15 μv/deg. C; at –100 C about 30, and at 0 C about 40, or nearly the same as for copper-constantan thermocouples in the same range. However, for temperatures below about 200 C the manufacturers of Chromel and Alumel recommend a thermocouple of Chromel X ($Ni_{64}Fe_{25}Cr_{11}$), and a variety of constantan designated as Copel ($Ni_{45}Cu_{55}$).

The most important applications of the Chromel-Alumel thermocouple are in the range of temperature from 1400 to 2300 F (700 to 1260 C), in atmospheres which are not reducing. It deteriorates rapidly at high temperatures in atmospheres containing hydrogen, sulfur or carbon monoxide. Products resulting from the reduction of metallic oxides in the insulators are probably responsible for the deterioration. Chromel and Alumel wires for industrial thermocouples are usually of either 8 gage, B & S (0.1258″ diam.) or of 14 gage B & S (0.06408″ diam.), the former being used for exposed thermocouples without protection tubes.

* *N.B.S. Circular 508, May, 1951.*

F. Copper-Constantan

1. Range

The copper-constantan thermocouple serves as a convenient and dependable means of determining temperatures down to liquid air temperatures (85K or –188 C) and with suitable precautions down to 11 K (–262 C). Its upper limit is about 350 C, being restricted by the oxidation of copper at higher temperatures.

2. Copper

Copper of high electrical conductivity and low oxygen content is very homogeneous, and gives a highly reproducible thermoelectric power against platinum. It need not be specially selected for thermocouple use if it conforms to ASTM Spec. B3-45 for Soft or Annealed Bare Copper Wire.

3. Constantan

Constantan is an alloy of copper and nickel of composition ranging from $Cu_{50}Ni_{50}$ to $Cu_{65}Ni_{35}$ but for thermoelectric purposes it has an approximate composition Cu_{57}, Ni_{43}, with addition of small percentages of Mn, and Fe as well as some trace impurities, such as C, Mg, Si, Co, etc. The precise composition of the alloy is not specified, but depends upon whether it is to be used with copper to match the copper-constantan table designed as "1921"* or the Adams "1938"** table. The manufacturer of the alloy adjusts the composition to give definite emfs against standard platinum at certain fixed points. "Adams constantan" is not specified as an alloy of definite composition, but is any copper-nickel alloy that combined with copper which conforms to ASTM B3-45 matches the Adams copper-constantan table.

An alloy of 60 copper with 40 nickel gives the greatest thermoelectric power against platinum of any of the constantans. Any departure from this ratio or any addition of other constituents tends to decrease the thermoelectric power. Small deviations from the 60-40 ratio have less effect on the thermal emf than similar deviations at any other ratio, since the curve of emf against percentage copper is flat at 60 per cent copper. It would, therefore, have been fortunate if the constantan chosen when establishing the copper-constantan tables had had a nominal 60-40 composition, with additions of manganese, and possibly of iron to improve working qualities. Constantan was originally developed as a resistance material with nearly zero temperature coefficient, and the 57-43 composition was adopted as giving most nearly the desired result. This is the constantan which was combined with copper (or iron) to give the existing temperature-emf tables, and was, unfortunately, not the best constantan for the purpose.

4. Calibration at Sub-zero Temperatures

The thermoelectric power of the copper-constantan thermocouple increases rather uniformly from about 15 μv/deg. C at –200 C to 60 μv/deg. C at 350 C. It has been found that the temperature-emf relation for a copper-constantan thermocouple in the range from 0 to –190 C may be expressed by the formula

$$E = at + bt^2 + ct^3$$

* *L. H. Adams, Pyrometry, p. 165 (Symposium published by A.I.M.M.E. 1920).*
** *Wm. F. Roeser and A. L. Dahl, N.B.S. Jour. of Res. Vol. 20, (1938) pp. 337-355.*

where E is the emf, t the temperature in degrees C and a, b, and c are constants which are computed by the method of least squares from observations of E at various well distributed values of t in the range from 0 to –190 C, for example, at 10 degree intervals. The values of E obtained by substituting in the above formula may be compared with the tabular values for the corresponding temperatures, and the differences plotted as a correction curve for reducing observed to true values of temperature. With a suitable constantan the correction curve should be smooth and the deviations should not exceed a few microvolts throughout the range.

5. Limits of Error

Since copper wires which conform to ASTM Spec. B3-45 are thermoelectrically alike to about a microvolt, the limits of error of copper-constantan thermocouples are set by the degree of reproducibility of constantan from melt to melt. Adams constantan is accepted for stock if it gives emf's against platinum which match tabular values within ± 0.5 per cent of the measured value. Copper-constantan thermocouples made of wires taken at random from stock will match, the 1938 N.B.S. temperature-emf table for copper against Adams constantan within limits of error of ± 0.5 per cent or ± 1.5 deg. F, whichever is larger, between –75 and +200 F. Between 200 and 700 F the limit is ± 0.75 per cent of the measured temperature. Those limits can be cut in half, or even less, by selecting constantan which matches tabular values more closely.

6. Applications

The copper-constantan thermocouple has been much used in industrial and laboratory applications for accurate measurement of temperatures between –200 and +350 C. Above 350 C the copper oxidizes too rapidly to give satisfactory service. In its range it is somewhat more satisfactory than the platinum thermocouple, because of its greater thermoelectric power, and also from the standpoint of cost. Since wires of sizes smaller than No. 22 B & S are usually employed, they can be installed in many places which are difficult of access, thus lending themselves very well to studies of temperature distribution in equipment. It has an advantage in this respect over the resistance thermometer, which is also much used in the same temperature range. As compared with the iron-constantan thermocouple it is preferable in its range because of the superior homogeneity of copper. Both iron and constantan tend to be inhomogeneous, producing parasitic emfs where a temperature gradient exists along the wire, which may introduce appreciable errors, particularly at temperatures below 200 F.

G. *Iron-Constantan*

1. General

Iron-Constantan thermocouples are the most widely used of all the thermocouples in industrial pyrometry. Well over two hundred tons of these thermocouple materials are supplied to industry annually in the U. S.

This is in spite of the fact that the use of iron as a thermocouple material was vigorously opposed by early workers in the field of thermoelectric pyrometry. Burgess and Le Chatelier in their book on "Measurement of High Temperatures" (1912) are emphatic on this point, basing their objec-

tions on the inhomogeneity of iron wires, and the consequent large parasitic emfs developed where a temperature gradient exists in the wire. Industry has found, however, that the relatively high thermoelectric power of the iron-constantan thermocouple, its comparatively low cost, and its adaptability to both oxidizing and reducing atmospheres justify its use. It has also been found that the iron wire which is now used in thermocouples is not appreciably less homogeneous than the constantan with which it is paired. When used under such conditions that the temperature gradient along the wire is not subject to rapid fluctuations the parasitic emf's seldom result in errors larger than a degree or two in the measured temperature.

2. Iron

Iron is not economically obtainable in as pure a state as is copper. "Commercially pure" irons contain small amounts of carbon, silicon, nickel, manganese, etc., all of which affect their thermoelectric properties. Electrolytic iron is costly and was not a commercial product at the time when iron-constantan thermocouples were being adopted by industry for pyrometric measurements. Consequently, at the time the L&N iron-constantan table was established in 1913 it was based on an available low carbon iron wire of the type which might have been used for rivets or for telegraph wire, combined with a constantan wire which was not very different from the Adams constantan referred to under Copper-Constantan in the preceding section. This table is still in use with minor revisions.

No difficulties were encountered in procuring iron for thermocouples so long as the limits of error were those involved in the use of millivoltmeters for the measurement of emf. A limit of error of ±10°C (18°F) at 1000 C was considered excellent and ±20°C (36°F) was acceptable for most industrial applications. But with the general introduction of the potentiometric methods of measurement in industry the difficulties in procurement of iron and constantan to match the standard temperature-emf curve well enough to take advantage of the higher precision of measurement made a serious study of the subject imperative.

N.B.S. Calibration Curve

At N.B.S. an extensive investigation was carried out and a temperature-emf curve was established for a thermocouple consisting of Adams constantan and a "mean" iron which resulted from determinations of the platinum-iron curve for some 19 samples of "commercially pure" iron as sold for use in thermocouples by various instrument companies. This curve which was published in 1938*, and which is referred to as the "RP1080" curve, was adopted by many government agencies and, in particular, was included in Joint Army and Navy specifications.

L&N Calibration Curve

It was considered impractical by L&N and by several other instrument companies to change all instrument scales and recorder charts in the field to conform to the "RP1080" curve and an investigation was undertaken to discover the composition of an iron to match the iron used in the establishment of the 1913 L&N I-C curve and to find sources of supply for such iron in

** Wm. F. Roeser and B. I. Dahl, N.B.S. Jour. of Res. 20 (1938) pp. 337-355. Reference Tables for Iron-Constantan and Copper-Constantan Thermocouples.*

large quantities. It is now possible to secure iron which matches the original iron within ± 0.5 per cent from 500 to 1500 F and within ± 33 μv below 500 F. Combined with a constantan with similar limits of error this results in a thermocouple with nominal limits of error of ± 1 per cent from 500 to 1500 F and of ± 66 μv below 500 F. Actually, acceptable wires give emfs which are closer than this to the L&N I-C conversion tables. Other instrument companies may arrive at the same result by the use of a slightly different iron, and a compensatingly different constantan.

N.B.S. Research Paper No. 2415, May 1953, presents I-C conversion tables which have been adopted as standard by the Scientific Instrument Makers of America. These tables do not differ significantly from the L&N 1913 I-C tables, abridged on pp. 82-83. Thus there are now two coexistent I-C standard tables; the "RP1080" used mainly by the armed service, and the "RP2415" intended for industrial use.

3. Constantan

The Adams constantan used with copper for thermocouples cannot be employed with iron, because of different voltage requirements. It is therefore necessary to use a constantan especially formulated for iron.

4. Applications

Iron-constantan thermocouples for heavy duty, for example in heat-treating furnaces where they are exposed directly to the furnace atmosphere or in protecting tubes of various materials are usually made up of No. 9 Birmingham gage (0.148″ diam.) iron wire, versus No. 8 B & S gage (0.1285″ diam.) constantan wire. They are serviceable in oxidizing atmospheres at temperatures up to about 1400 F where they have a life of about 1000 hours. They may also be used in reducing atmospheres, up to about 1800 F, not being subject to the deterioration that occurs with chromel-alumel thermocouples in reducing atmospheres. For lighter duty, No. 14 B & S gage (0.06408″ diam.) iron and constantan wires are often used, while for laboratory applications the even numbered B & S gages of iron and constantan wire are available from 14 to 30 gage inclusive.

H. Miscellaneous Thermocouples

Many combinations of conductors for thermoelectric pyrometers are available which have not been put to as general use as the ones described above.

1. Chromel Constantan

Chromel-Constantan is a combination with excellent properties, both elements being resistant to corrosion and capable of operating at temperatures up to 2000 F. It has been much used in thermopiles for radiation pyrometers where its high thermoelectric power is of advantage. It is sometimes used in place of chromel-alumel in industrial thermocouples.

2. Chromel-White Gold

For use in thermopiles a combination of chromel with an alloy of $Au_{90}Ni_{10}$ is somewhat superior in thermoelectric power to chromel-constantan, and has been used to a limited extent for this purpose.

3. Chromel-Stainless Steel

Stainless steel (KA2S) has occasionally been used in place of alumel in

industrial thermocouples, but seems to have no outstanding advantages, except in atmospheres containing sulfur.

4. Nickel-Nickel Molybdenum

Nickel against nickel-molybdenum has been used in some applications.

5. Molybdenum-Tungsten

Molybdenum against tungsten has been used to measure the temperature of molten steel. The thermoelectric power is very low, and reverses at about 600 C. Both metals oxidize readily at high temperatures and must be used in a protecting tube.

6. Graphite-Silicon Carbide (Fitterer)

A couple consisting of a rod of silicon carbide supported by insulators inside a tube of graphite and imbedded in it at the hot end has had some use in molten metals. This thermocouple gives a very high but not very reproducible thermoelectric power. The graphite dissolves rapidly in molten steel requiring frequent replacement. It gives much better service in high carbon iron. A coating of lime slurry aids in prolonging its life.

7. Tungsten-Graphite

A tungsten-graphite couple has also seen some service in molten metals. Its thermoelectric power is very low at room temperatures, but increases to reasonably high values above 2000 F. As a result "cold junction" corrections are very small.

8. Tungsten-Iridium

This thermocouple, described in U. S. Patent 2,588,998, is said to be usable up to 2100 C producing an emf of over 40 mv. at this temperature. It has a negligible emf from 0 to 100 C and hence requires no reference junction compensation. It has been exposed to temperatures up to 2000 C for 120 hours in a helium atmosphere without appreciable deterioration.

9. Nickel as a Constituent of Thermocouple Alloys

It may be worth noting that nickel is a very important constituent of most of the base metal thermocouple materials. Constantan contains from 40 to 50 per cent nickel; chromel P, 90 per cent; alumel, 95 per cent. The copper and iron elements are the only ones that contain no significant amount of nickel. Pure nickel would probably have been used in place of alumel if its thermoelectric power against platinum had followed a smooth curve through the range from 230 to 390 C. Nickel and its alloys are subject to intergranular corrosion in hot gases containing sulfur, resulting in weakening and eventual premature failure of constantan, chromel and alumel wires. Sulfur in the form of SO_2 is a common constituent of combusted gases, and often an unsuspected one, and accounts for numerous failures of thermocouples in furnace atmosphere. It would be desirable to produce an alloy to replace constantan in which the sulfur attack is inhibited.

chapter 3

Fabrication of thermocouples

A. Platinum-Platinum +10% Rhodium

A typical industrial $Pt\text{-}Pt_{90}Rh_{10}$ thermocouple is fabricated as follows:

1. Choice of Wires

The No. 24 B & S gage CP platinum and the platinum-10-per-cent-rhodium wires are received from the supplier as reels of wire about five inches in diameter and have been fully annealed by the supplier. A sample of the CP platinum is welded to a standard platinum wire and the junction placed in a furnace at about 1800 F. The other ends are connected to a low resistance galvanometer. If a deflection corresponding to more than a few microvolts is observed, the reel of nominally CP platinum is unsuitable for use. A similar test is made on the $Pt_{90}Rh_{10}$ wire, against a standard $Pt_{90}Rh_{10}$ wire.

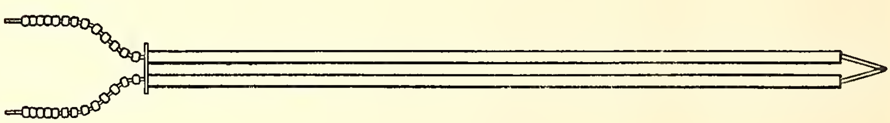


Fig. 10 Thermocouple Assembly of $Pt\text{-}Pt_{90}Rh_{10}$

2. Welding and Assembling

Suitable lengths of the two wires are cut off and butt welded together at one end by means of a carbon arc; no flux is used and the wires are not twisted together. The junction is a small smooth bead. The thermocouple is sometimes sent to the user in the form of an uninsulated open coil, but more commonly the wires are insulated from each other by means of single hole ceramic insulators in unbroken lengths of several inches, extending as close as possible to the weld. When the wires are too long to be covered with a single length of insulator, care is taken to stagger the breaks, so that a break in the insulator covering one wire shall not be adjacent to a similar break on the other wire. For the sake of flexibility the last two or three inches of the wires, after passing through a ceramic button, are threaded through fish-spine insulators, up to where the wires are attached to binding posts in the "head." Throughout these operations care is taken to bend or otherwise cold-work the wires as little as possible. The structure is usually protected by placing it in an unglazed porcelain tube. Protection tubes will be discussed in chapter 4.

In fabricating thermocouples from 26-gage or finer wires, the maker may prefer to weld with an oxy-hydrogen flame instead of an electric arc. By either method, there is an acquired "knack" in producing strongly-welded thermocouples of correct emf.

3. Renovation of Contaminated or Inhomogeneous Thermocouples

A platinum thermocouple which has been made inhomogeneous by cold working or thrown off calibration by some forms of contamination may be reconditioned by heating for a few minutes to a temperature of about 2300 F (1200 to 1300 C) to relieve strains and to oxidize impurities. The annealing temperature should be higher than the temperature to be measured.

Metallic oxides and reduced metals may be removed by allowing a molten bead of borax to flow down the heated wire. The cleaned thermocouple should not be touched with bare fingers, since grease or graphite deposited on it may result in contamination when heated. If it is inadvertently handled, it should be washed with alcohol and wiped with clean filter paper. The ceramic insulators removed for the purpose of cleaning the wire, should be cleaned by boiling in alcohol and heating to redness in a furnace before replacing them on the wire. Better yet, use new, clean insulators.

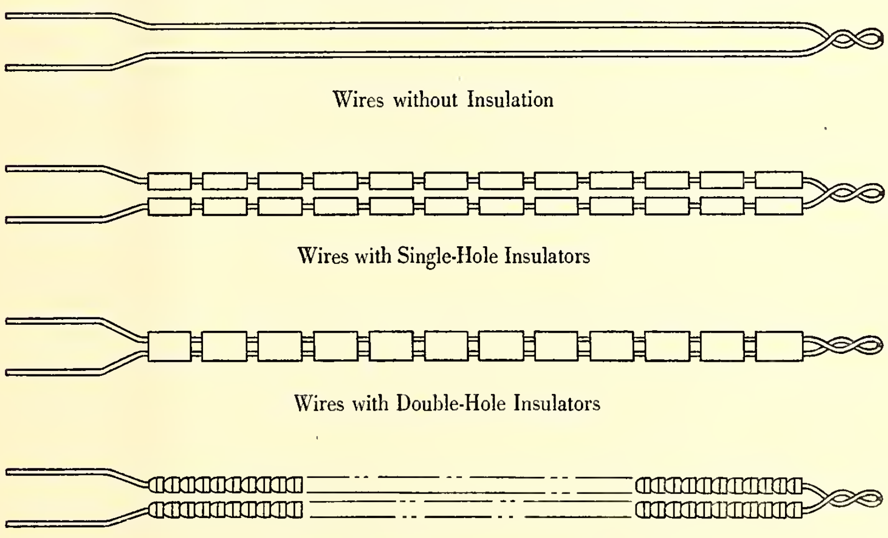


Fig. 11 Thermocouple Assemblies of Chromel-Alumel or Iron-Constantan

B. Chromel-Alumel

In making up a thermocouple of Chromel and Alumel, wires of the two materials are chosen which have been found by inspection tests to match the standard Chromel-Alumel table. The wires as taken from the coil are cut to length and straightened; the cold working involved in straightening is not sufficient to produce appreciable inhomogeneity. The ends of the two wires are firmly but carefully twisted together through about two complete turns, and the

weld is formed by means of a d-c carbon arc, using borax or fluorspar as a flux. Alumel melts at a slightly lower temperature than Chromel, and it is necessary to manipulate the arc so that the heat is applied more directly to the Chromel than to the Alumel so that both will melt at the same time and the two metals flow together. The melting and welding should be accomplished quickly and with a minimum of flow, forming a smooth, well rounded bead. In the production of commercial thermocouples the twisting is done in a machine which is adjusted to give the proper number of close turns, but without straining the wire excessively. Strains beyond the elastic limit open up cracks, and shorten the life of the couple. The two wires are insulated from each other by means of porcelain beads or short ceramic tubes and are usually inserted in a suitable protecting tube provided with a (generally weatherproof) head for attachment of extension wires.

Chromel-Alumel thermocouples made of wire smaller than No. 14 B & S are often welded in the oxy-acetylene flame.

C. Copper-Constantan

Since copper-constantan thermocouples are used only for measuring temperatures not over 500 F, the formation of measuring junctions by autogeneous welding is not often resorted to in fabricating them. The junctions are usually silver-soldered, but for low temperature work may be soft-soldered. Care must be taken to remove all trace of flux. The wires are not ordinarily twisted together near the junction. In the range of temperatures in which these thermocouples are ordinarily used it is not necessary to use ceramic insulators. Often enameled wires are used or enamel with a covering of silk or cotton. Where measurements are to be made at temperatures too high for these materials a covering of fibre glass may be used.

D. Iron-Constantan

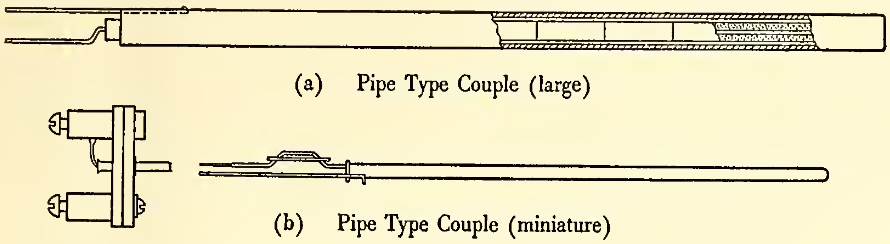
1. Wire Type Couples

The procedures described for the chromel-alumel thermocouples in general apply equally well to thermocouples of iron and constantan wire. (See page 21.)

2. Pipe-Type Couples

Pipe-type thermocouples of iron and constantan are much used in the measurement of furnace temperatures. Such a thermocouple is made up of a tube of wrought iron, within which is placed a constantan wire, separated from the tube with ceramic insulators. The constantan wire is welded to an iron plug which fits into one end of the tube. After inserting the insulated wire with the attached plug, the plug is welded to the tube, making a gas-tight seal. The constantan wire projects from the open end of the tube and forms one terminal. An iron wire welded into a slot cut in the open end of the tube forms the other terminal of the thermocouple. In its larger form the iron tube is extra-heavy $3/8''$ pipe ($11/16''$ O.D.) and the constantan is a No. 8 B & S gage wire. The exterior of the tube is usually protected against oxidation by spraying with nichrome, forming a protective coating about 0.01″ thick. (Fig. 12 A)

The miniature pipe-type thermocouples (Fig. 12 B) used principally in laboratory work and in pilot plants, are made up of $1/8''$ O.D. seamless iron



(a) Pipe Type Couple (large)

(b) Pipe Type Couple (miniature)

Fig. 12 Pipe-Type Thermocouples

tubing enclosing a No. 20 B & S gage constantan wire, well insulated from the tube with asbestos or with fiber glass, and welded into the end of the iron tube, forming a closure. The exterior of the tube may be bare or protected with a thin coating of chromium.

chapter 4

Installation of thermocouples

A. General

The emf generated by a calibrated thermocouple is a measure of the difference of temperature of the measuring junction and the reference junction. If the reference junction temperature is known and fixed, a measurement of emf makes it possible to compute the temperature of the measuring junction. If it is desired to use a thermocouple to measure the temperature of a hot body, such as a steam pipe, or the steam inside the pipe, it is necessary to assume that the measuring junction is at the temperature of the pipe or of the steam. Too often this assumption is incorrect where suitable precautions have not been taken in the installation of the thermocouple. The thermocouple wires conduct heat away from the junction tending to make it cooler than the pipe, or, in the steam, heat is lost by radiation to the cooler walls of the pipe and again the junction is cooler than the steam. Or the junction may be placed in a protecting tube of considerable heat capacity, and will respond slowly to fluctuations in the temperatures of the medium in which the tube is placed.

If the thermocouple could be made of such thin wires that heat conduction along them and radiation to or from them could be neglected, and of such durable materials that no protection tubes were necessary, the junction would be at the temperature to be measured. Unfortunately, this ideal thermocouple is not available and the user of a practical thermocouple is always confronted with the fact that it is the temperature of the junction and not necessarily that of its surroundings that is being measured.

B. Installation of Bare Thermocouples

In some applications it is possible to expose the thermocouple wires and the junction directly to the atmosphere in which it is used without a protecting tube. In many laboratory applications, at temperatures below about 200 C thermocouples made up of wires insulated with enamel, cotton, silk, or glass fiber and without other protection give very satisfactory service. Some of the precautions to be observed are described below:

1. In Solids

When measuring the temperature of a solid, for example a metal tube, the junction must make intimate contact with the metal. This is sometimes accomplished by drilling a shallow hole in the metal just large enough to receive the junction, and then peening the junction firmly in place. The wires of the thermocouple tend to affect the temperature at the junction by carrying away

heat if they are cooler than the tube, or bringing heat to it if they are hotter. This effect may be reduced by wrapping the insulated wires around the pipe or tying them longitudinally to the pipe for a few inches. The junction is sometimes attached by means of a patch of adhesive material. A possible source of error here is the screening effect of the patch, which may tend to either lower or raise the temperature of the surface beneath it, depending upon whether the pipe is receiving heat from its surroundings or losing heat to them.

2. In Gases

When measuring the temperature of gas in a conduit, radiation becomes a serious source of error if the walls of the conduit are either warmer or cooler than the gas. If the walls are warmer than the gas, a junction in the gas stream is heated above the temperature of the gas even when the gas is flowing vigorously past the thermocouple. The error introduced decreases as the size of the thermocouple is reduced, and as the rate of flow is increased. If the thermocouple is surrounded with a radiation shield of polished metal, so that it cannot "see" the walls of the conduit, the error is greatly reduced. A further improvement results if the gas is forced to flow through the radiation shield at high velocity. The radiation shield is sometimes made up of two or three coaxial cylinders so as to bring the inside of the inner shield as close as possible to the temperature of the gas.

3. In Electrolytes

Wire thermocouples must not be used bare in electrolytes, even if they are not attacked by the solution. The electrolyte will act as a partial short circuit on the thermocouple circuit, reducing the apparent emf. A still worse source of error may be the electrolytic emf set up between the wires. The pipe-type couple can be used in such application, since only one of the components is exposed to the electrolyte.

4. In Heat-Treating Furnaces

Bare iron-constantan and chromel-alumel thermocouples are used extensively in heat-treating furnaces. In the former the constantan wires are usually No. 8 B & S gage and the iron is No. 9 Birmingham gage, having about 30 per cent greater area of cross-section than the constantan. This serves to compensate to some extent for the fact that the iron oxidizes more rapidly than constantan. When used in the heat-treatment of carbon steel in air by quenching from a temperature slightly above its transformation point (usually between 1300 and 1400 F), such a thermocouple has a useful active life of about 1000 hours. The use of a protecting tube for the thermocouple in this process would make the response too slow to detect passage of the work through its transformation point. It is necessary for the junction to make actual contact with the material being heat-treated to secure the prompt response to changes of temperature required to make the break in the time-temperature curve distinct.

5. In Molten Metals

The temperature of a molten metal is sometimes measured by dipping the ends of the suitably supported bare thermocouple wires in the molten metal, thus closing the circuit through the thermocouple. The immersed ends then become the measuring junction and the temperature is readily determined. After each immersion the ends are cut off and discarded, a fresh, uncontaminated portion of the wire being used for each measurement. The temperature

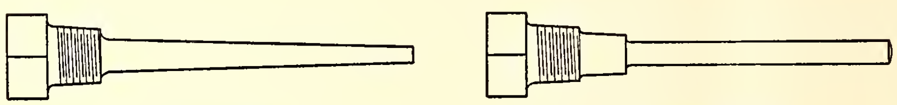
measured is that close to the surface of the molten metal.

C. Thermocouples in Protecting Tubes or Wells

With few exceptions, some of which are mentioned in the preceding paragraph, the thermocouples used for industrial applications are enclosed in either protecting tubes, or in wells. Protecting tubes are used for installations at close to atmospheric pressure, or if of metal and equipped with pipe thread bushings may be used at pressures somewhat above atmospheric. Protecting tubes, particularly for platinum thermocouples, are often ceramic materials, such as mullite, porcelain, sillimanite or silicon carbide.

1. Wells

Protecting wells are used in liquids or gases at high pressures. Their use is imperative at pressures above about 50 pounds per square inch, though they may be used at lower pressures. They are always of metal, and may be turned and drilled from bar stock in one piece, Fig. 13a, or built up of a tube, a plug, and a hexagonal head with all joints welded, Fig. 13b. Drilled wells are



(a) Drilled Well

(b) Built-up Well

Fig. 13 Thermocouple Wells

recommended for pressure above 500 pounds per square inch. Depending upon the service for which they are intended, wells are usually fabricated of carbon steel, stainless steel (18 & 8) or 14 per cent chromium iron.

2. Protecting Tubes

The protecting tube serves the double purpose of guarding against mechanical injury and of interposing a shield between the thermocouple and its surroundings so as to maintain it as nearly as possible in its best atmosphere. As has been pointed out, thermocouple materials are subject to deterioration and contamination in unfavorable surroundings. They have been chosen on the basis of their behavior in air, and to get the best results from them they should operate in pure dry air. The function of the protecting tube is to maintain the proper atmosphere around the thermocouple by excluding injurious materials while at the same time offering a ready means for heat-transfer between the thermocouple and the region outside the protecting tube.

The agencies which may need to be excluded are such as: (a) Metals (solid, liquid, or vapor) which, coming into contact with the thermocouple, would alter its chemical composition, (b) Furnace gases and fumes which may attack the thermocouple materials (Sulfur and its compounds are particularly deleterious), (c) Materials such as silica and some of the metallic oxides, which, in contact with the thermocouple in a reducing atmosphere, are reduced, and combine with the thermocouple material to contaminate it, (d) Electrolytes which would attack the thermocouple material, or form an electrical connection between the wires, or set up a battery action.

a. In Molten Metals

In selecting tubes for use in molten metals, various hazards must be overcome. Metals which alloy with the bath, or are attacked by the slag, should be avoided. Ceramic tubes are ruled out if the heat-shock is severe. Tubes of silicon carbide or graphite are not limited in these ways, but they may need such thick walls for mechanical strength that the resulting lag becomes too great. And some materials dissolve in others, as graphite in low-carbon steel.

However, careful engineering has solved many specific problems. Here are a few examples:

In molten aluminum, grey cast iron protecting tubes of 1/4 inch wall thickness and coated with lime slurry or other coating material have given satisfactory service. In molten copper, a chromel-alumel thermocouple in a graphite protecting tube is sometimes used, giving a useful life of about 200 one-minute immersions at temperatures below 2350 F. Temperatures of molten steel and nickel are measured with platinum thermocouples, protected by small fused-quartz tubes. One tube is needed for each immersion, but the fixture may be designed so as to make this replacement easy and rapid.

A chromel-alumel thermocouple in a protecting tube of cast nickel-chrome has a useful life of 5 to 6 months at 1550 to 1600 F in baths of molten lead.

For temperatures below 900 F in lead baths, iron-constantan thermocouples in wrought iron or 28 per cent chrome-iron protecting tubes give from 6 to 10 months' continuous service. In tin, at 625 to 650 F, thin-walled steel protecting tubes enclosing iron-constantan thermocouples last for several weeks. For molten magnesium, protecting tubes of extra heavy seamless low carbon steel are suitable. In molten silver, chromel-alumel thermocouples in iron protecting tubes are good for about 500 short immersions at 2000 to 2300 F.

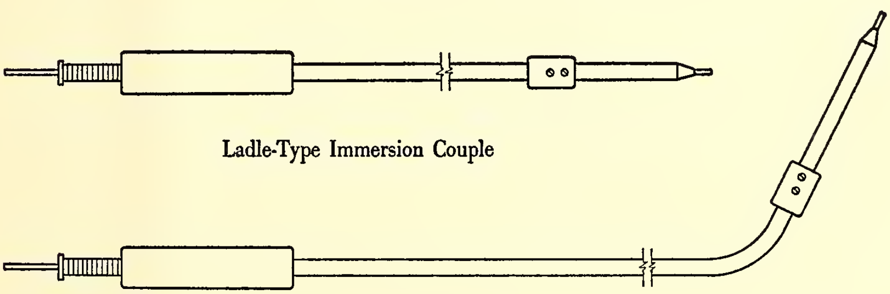


Fig. 14 Types of Immersion Thermocouples

b. In Furnace Atmospheres

Where protecting tubes are used in furnace atmospheres to prevent corrosion or contamination of thermocouples, there is a fairly wide choice of materials. Metal tubes of various sorts are very widely used, for the sake of their superior resistance to thermal and mechanical shock, but for the protection of platinum couples at temperatures above 2300 F, heat resistant porcelain tubes are required. These are usually unglazed, though glazed tubes are also supplied, being less pervious to furnace gases. It is well known that platinum is particu-

larly vulnerable to contamination in hydrogen or carbon monoxide and glazed mullite porcelain (Fyrestan) gives the best protection of any of the available tube materials. But even this material at high temperatures is readily penetrated by hydrogen, and is not an adequate protection for the thermocouple. In such applications the substitution of the Rayotube for the thermocouple is recommended. In some cases a P.B. Sillimanite secondary tube serves to protect the gazed Fyrestan tube, giving more mechanical protection and further impeding the penetration of hydrogen. This makes the element very slow in responding to temperature changes, and does not provide complete protection.

Even at lower temperatures, with chromel-alumel thermocouples in metal tubes, both CO and H diffuse through the walls rapidly enough to throw the thermocouple off calibration appreciably in a few minutes. Chromel-alumel thermocouples should not be used in a reducing atmosphere even when apparently well protected. Here again the Rayotube should be used at least for temperatures above 1400 F. Below this temperature iron-constantan is sufficiently stable and adequately protected by metal protecting tubes.

c. *In Salt Baths and Chemical Processes*

The choice of protecting tubes for use in baths of brines, acids, caustics, and for chemical processes in general is a matter for the chemist in charge of the process to decide, with the aid of information from the following tables of tube materials. If the process vessel in which the protecting tube is to be placed is of metal, the tube should be of the same metal in order to minimize electrolytic corrosion.

D. Ceramic Tube Materials

1. L&N Fyrestan

Fyrestan is a highly refractory mullite porcelain, normally used for primary protection and often for secondary protection. It can be obtained unglazed or glazed, the latter form being more impervious to gases. Having a softening point of about 3000 F, tubes of L&N Fyrestan can be mounted vertically at a temperature of 2800 F. When mounted horizontally, the recommended maximum temperatures are 2750, 2650, 2500, and 2300 F for unsupported lengths of 3, 6, 12 and 18 inches respectively.

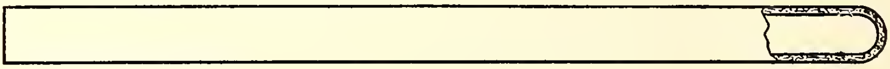


Fig. 15 Fyrestan Protecting Tube

2. Silicon Carbide Refractory

Tubes of silicon carbide refractory are used for secondary protection at temperatures up to 3000 F. It is highly resistant to the cutting action of flames and gases.

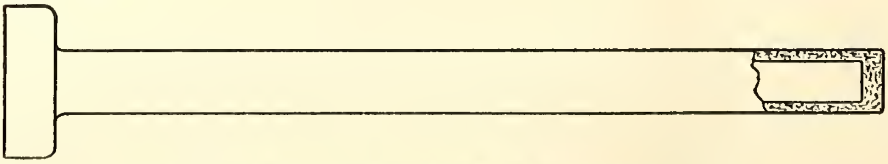


Fig. 16 Silicon Carbide Protecting Tube with Collar

3. P. B. Sillimanite

Tubes of this material are also highly resistant to erosion from flames and gases and are used for secondary protection at temperatures as high as 3000 F.

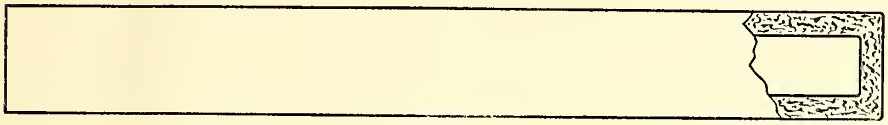


Fig. 17 P.B. Sillimanite Secondary Protecting Tube

E. Metal Tube and Well Materials

Metal protecting tube and well materials described below are, in general, arranged in the order of their increasing resistance to oxidation, increasing mechanical strength at elevated temperatures, and increasing upper limit of useful temperature. Figures in parentheses are recommended maximum temperatures.

1. Carbon Steel

(1000 F) Satisfactory in any except corrosive atmospheres.

2. Wrought Iron

(1300 F) Satisfactory in any except corrosive atmospheres. Often used in non-corrosive atmospheres at temperatures as high as 1500 F, as fairly frequent replacement at low cost may be more advantageous than the use of an alloy.

3. Cast Iron

(1300 F) Generally more useful than wrought iron in the chemical industry. Resistant to concentrated sulphuric acid and caustic solutions.

4. Metal-Sprayed Wrought Iron

(1500 F) More resistant to corrosion than wrought iron. Principally used for pipe-type couples.

5. 14% Chromium Iron

(1500 F) Resistant to chemical corrosion, particularly sulphur.

6. 28% Chromium Iron

(2000 F) Extensively used as a general purpose alloy tube. In general, more resistant to corrosion than 14% chromium iron. Also highly resistant to sulphur attack.

7. 18% Chromium-8% Nickel

(1600 F) Resistant to corrosion. Generally used for protecting wells in wet process applications such as steam lines, oil refineries and chemical solutions.

8. 32% Nickel-20% Chromium

(2000 F) For general high temperature use except in sulphurous atmospheres. Has greater mechanical strength than the 28% chromium iron and 18% chromium-8% nickel. More resistant to sulphur than higher nickel alloys, but less resistant than 28% chromium iron.

9. 62% Nickel-13% Chromium

(2100 F) More resistant to oxidation than 32% nickel-20% chromium.

10. Nickel

(2100 F) Principally used for hot caustic and molten salt baths.

F. Guide to Tube and Well Materials for Specific Applications

1. Heat Treating

Annealing, Drawing and Tempering (Air or Protective Atmosphere)
Up to 1300 F—Wrought Iron
1300 to 1500 F—28% Chromium iron or wrought iron
Over 1500 F—28% Chromium Iron

Carburizing
62% Nickel-13% Chromium

Hardening
Up to 1500 F—Wrought iron or 28% chromium iron
1500 to 2000 F—28% Chromium iron or 32% nickel-20% Chromium
Over 2000 F—Fyrestan, or use Rayotube in place of couple

Nitriding
62% Nickel-13% Chromium

Salt Baths
Nickel (28% chromium iron satisfactory for cyanide)

2. Iron and Steel (Making and Working)

Annealing
Up to 1300 F—Wrought Iron
1300 to 1500 F—28% Chromium iron or wrought iron
Over 1500 F—28% Chromium iron

Blast Furnaces
Down-Comer—62% Nickel-13% Chromium
Hot Blast Main—62% Nickel-13% Chromium
Stove Dome—Use Rayotube in place of couple
Stove Trunk—62% Nickel-13% Chromium

Billet Heating, Brazing, Patenting, Butt Welding
Slab Heating
Up to 2000 F—28% chromium iron, 32% nickel-20% chromium or 62% nickel-13% chromium
Over 2000 F—Fyrestan, silicon carbide refractory, or use Rayotube in place of couple

Bright Annealing
Batch—No protecting tube (use bare iron and constantan couple)
Continuous—Glazed Fyrestan, or use Rayotube in place of couple

Forging
Fyrestan, or use Rayotube in place of couple

Galvanizing Baths
Carbon Steel or silicon carbide refractory

Open Hearths
Air Flue—28% Chromium iron
Checkers—28% Chromium iron (in cold zone)
or use Rayotube in place of couple
Roof—Use Rayotube in place of couple
Waste Heat Boiler—28% Chromium iron

Soaking Pits
Up to 2000 F—28% Chromium iron, 32% nickel-20% chromium or 62% nickel – 13% chromium
Over 2000 F—Fyrestan, silicon carbide refractory,
or use Rayotube in place of couple

3. Non-Ferrous Molten Metals
Aluminum
Cast iron (whitewashed)

Lead
Wrought iron, 28% Chromium iron or 62% nickel-13% Chromium

Magnesium
Wrought iron or cast iron

Tin
18% Chromium-8% Nickel or carbon steel

Zinc
Carbon Steel or silicon carbide refractory

4. Portland Cement
Flues
28% Chromium iron or 62% nickel-13% chromium

Kilns
Use Rayotube in place of couple

5. Ceramic
Brick Kilns
Fyrestan (primary); silicon carbide refractory or P.B. Sillimanite (secondary); or use Rayotube in place of couple

Ceramic Kilns
Continuous
Fyrestan (primary); Fyrestan or silicon carbide refractory (secondary); or use Rayotube in place of couple

Periodic
Fyrestan (primary); P.B. Sillimanite (secondary)
or use Rayotube in place of couple

6. Chemical
Acetic Acid
28% Chromium iron or 18% chromium-8% nickel

Brines
Nickel, or 28% chromium iron, or 18% chromium-8% nickel

Caustics
Cast iron, nickel or 18% chromium-8% nickel

Fatty Acids
18% Chromium-8% nickel-3% molybdenum

Hydrochloric Acid
Lead-covered tube or glazed Fyrestan

Mixed Acids, Fruits, Lactic, Hydrocyanic Acid
Cyanogen Gas and Dyeing Tanks
18% Chromium-8% nickel

Nitric Acid
28% Chromium iron or 18% chromium-8% nickel

Phosphoric Acid
28% Chromium iron or 18% chromium-8% nickel

Sulphuric Acid
Dilute
Lead-covered tube or cast iron

Moderately Dilute
Lead-covered tube

Concentrated
Cast iron or 18% chromium-8% nickel

SO_2-Air Mixtures
28% Chromium iron

7. Glass
Flues and Checkers
28% Chromium iron

Forehearth and Feeders
Fyrestan

Lehrs
Wrought iron

Tanks
Fyrestan (primary); silica block in furnace roof (secondary); or use Rayotube in place of couple

8. Paper
Digesters
28% Chromium iron or 18% chromium-8% nickel-3% molybdenum

9. Petroleum
Dewaxing, Tower and Transfer Lines
Carbon steel or 18% chromium-8% nickel

Fire Box
28% Chromium iron or 62% nickel-13% chromium

Pilot Plants
Miniature pipe-type couples

10. Power
Coal-Air Mixtures
18% Chromium-8% nickel

Flue Gases
Wrought iron or 28% chromium iron

Preheaters (Air)
Wrought Iron

Steam Lines
18% Chromium-8% nickel

Water Lines
Carbon steel

11. Unclassified
Gas Producers
28% chromium iron

Incinerators
Up to 2000 F—28% chromium iron, or 32% nickel-20% chromium, or 62% nickel-13% chromium
Over 2000 F—Fyrestan (primary). If necessary, silicon carbide refractory (secondary)

G. *Installation of Thermocouple in Protecting Tube*

1. Insulation

The wires constituting a thermocouple must be well insulated from each other and from the walls of the metal protecting tube. The type of insulation may depend upon the temperature to which the tube is to be exposed. For low temperatures, wires insulated with enamel, cotton, silk, or glass fiber may be used, while for general purposes, at either high or low temperatures, porcelain insulators are universally serviceable. They may be in the form of single-hole or double-hole beads, of single-hole or double-hole tubes, or, where flexibility is required, of "fish-spine" insulators, which are convex at one end and concave at the other. In a metal protecting tube or well the junction should not be allowed to make electrical contact with the well, since such a contact might constitute a "ground" on the measuring circuit, and be a potential source of error, since other grounds may develop on the measuring circuit, or if the emf of more than one thermocouple is being measured by the same instrument, a cross-connection between the thermocouples may result.

2. Head

Usually the thermocouple wires terminate in a head which is firmly attached to the protecting tube, and which provides a means of attachment of the lead wires to the measuring instrument. The connection between thermocouple and lead wires should be made by means of some sort of screw clamp or binding post, to provide for ready replacement of thermocouple or of lead-wires. If the head is likely to become very hot, as in the case of a protecting well in a

high-pressure steam line, it is desirable to terminate the thermocouple wires two or three feet beyond the head, and connect with the leads at a junction box in a less hot location. It is preferable that the junction between thermocouples and leads should not be at a temperature above 200 F, since if the leadwires do not closely match the thermocouple wires, the junction may form a secondary source of emf introducing an error in the temperature measurement which increases with the difference of temperature between thermocouple and the instrument ends of the lead wires. However, head temperatures as high as 400 F are sometimes tolerated.

H. Installation of Protecting Tubes in Furnaces

Tubes and wells must be selected for correct ratio of diameter and length, in order to prevent drooping. These ratios are available from instrument manufacturers, and are especially important in the case of ceramic tubes inserted horizontally into very hot furnaces.

The depth of immersion of the protecting tube into the furnace should be enough to assure that the temperature of its tip is not affected by conduction of heat between the tip and the walls. With a metal tube it is particularly important to make the depth of immersion great enough. A test may be made in a furnace at a steady temperature, observing apparent changes in temperature when the tube is moved in or out. As it is moved in a depth should be reached beyond which no change in apparent temperature is observed as the depth of immersion is increased. This depth of immersion should be used if possible.

The temperature of protecting tubes is strongly affected by radiation from the furnace walls, and will generally be different from the temperature of the furnace atmosphere if the latter differs materially from that of the walls. To measure atmosphere temperatures, some variety of high-velocity, radiation-shielded protection tube should be used.

chapter 5

Extension wires for thermocouples

A. Purpose of Extension Wires

It is not usually convenient to locate the measuring instrument of a thermocouple close to the position where the thermocouple is being used. In laboratory measurements, it is a simple matter to connect copper leads to the ends of the thermocouple wires, with the junctions held at constant temperature in vacuum bottles of melting ice. These copper leads are then extended to the measuring instrument, their length being limited only by the resistance which they introduce in the measuring circuit. In industrial applications, where it is impractical to use ice baths, it is customary to employ "automatic cold-junction compensation" (See page 56).

The compensator is usually located at the measuring instrument, and the thermocouple wires should extend to the instrument. However, thermocouple wires are not generally suited for use as lead wires to extend for considerable distances. No. 8 chromel and alumel or iron and constantan wires are too cumbersome and expensive and not properly insulated for such a purpose.

Therefore, chromel-alumel and iron-constantan pairs are made up for extension-wire purposes, as duplex conductors, in smaller gages. Chromel and alumel are available as No. 16 gage, and iron and constantan as Nos. 14, 16, 20, 24, and 30 gages. The same sizes can also be supplied as single insulated conductors. Since the extension wires are not, except by remote chance, drawn from the same ingots as the thermocouple wires, the two sets of wires are not exactly

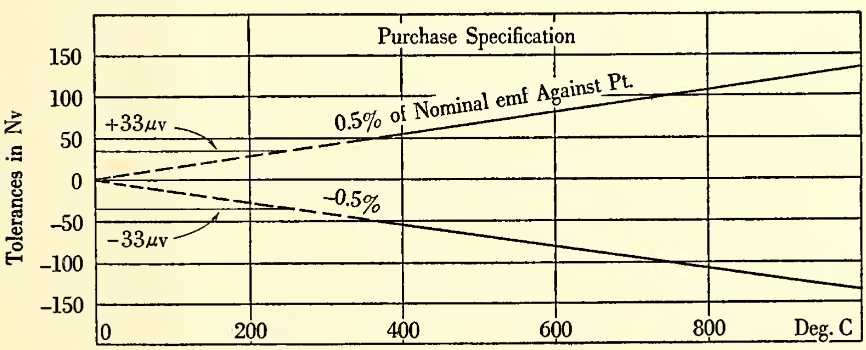


Fig. 18 Tolerances for Iron or Constantan Thermocouple Wire

alike in thermoelectric characteristics. The tolerances allowed in the acceptance of iron or constantan for thermocouples is ± 33 μv departure from the tabular

values for iron against platinum and constantan against platinum respectively, in the range of temperatures below 500 F. (Fig. 18) If the extension wires are drawn from bar stock which has passed this acceptance test, they may, at least theoretically, fall anywhere within these tolerances. We will examine the errors that may be introduced by such extension wires.

B. Errors Introduced by Extension Wires

Let us assume that an iron-constantan thermocouple with its measuring junction at a temperature T_M and its reference junction at T_R, produces an emf E which agrees with the value from the I.C. table; i.e., it is without error at these values of T_M and T_R. If the wires are continuous between measuring and reference junctions the magnitude of E is unaffected by the fact that the wires pass through regions of various temperatures. But if extension wires are used between the head and the reference junction, errors may result if the temperature of the head T_H, differs from T_R. Extreme cases are as follows:

a. At T_H the iron of the thermocouple has its maximum permissible error, +33 μv, against platinum, while the constantan also has its maximum error of —33 μv, (33 μv more negative against platinum than standard constantan). If the extension wires have no error at T_H the observed value of E is in error by +66 μv.

b. At T_H the extension wires have an error of —33 μv for the iron and +33 μv for the constantan while the thermocouple wires have the same errors as in (a); i.e., +33 μv for the iron and —33 μv for the constantan. The error in E becomes —132 μv for the thermocouple wires of (a).

c. If the characteristics at T_H of thermocouple and extension wires were reversed from those given in (b) the error would be +132 μv, or roughly 4 degrees F.

These are maximum and very improbable values for the error that may be introduced as the result of using extension wires randomly selected from material acceptable for thermocouples. To attain this value it is necessary that (a) the thermocouple wires individually depart from the standard tables by 33 μv at T_H and in opposite directions; (b) that the maximum departure of the extension wires shall also occur at T_H, and have the same magnitude as for the thermocouple wires, but of opposite sign. It is safe to say that the most careful selection from every melt of iron and of constantan that has ever been accepted for thermocouple purposes would not yield such a combination.

A study of the calibration curves for acceptable irons and constantans shows that a more reasonable value for the maximum error resulting from extension wires selected at random from thermocouple stock is more nearly 60 μv (2 degrees F) than the 132 μv computed above.

The situation is much the same for chromel and alumel extension wires as for iron and constantan.

To be satisfactory for extension wire purposes the pair needs to match the thermocouple wires closely only in the limited range of possible values of T_H and T_R. Outside this range the wire materials may depart much too widely from the standard tables to be acceptable as thermocouple material and still be

entirely satisfactory for extension wires. By selection based on checks at temperatures below 500 F it is possible to use for extension wire some melts which have been rejected as thermocouple material on the basis of too wide departures from tabular values at higher temperatures. Since for the sake of economy it is a common practice to make up extension wires from such rejected ingots, it is unwise to make use of extension wires as thermocouples for temperatures higher than 500 F.

C. Extension Wires of Materials Unlike Associated Thermocouple Wires

Extension wires of platinum and platinum 10 per cent rhodium are very expensive if there is any considerable distance between thermocouple head and measuring instrument. For precise work, ice baths are used at the head and the lead wires from there on are of copper. But for industrial applications, where recording of temperatures makes automatic reference junction compensators necessary, extension lead wires have been developed which match the platinum-platinum 10 per cent rhodium emfs very closely in the range of probable values of T_H and T_R. These consist of a copper wire and a wire of an alloy of nickel and copper, and are entirely adequate for industrial measurements.

There is no substitute for copper and constantan as leads for copper-constantan thermocouples, or for iron and constantan as leads for iron-constantan thermocouples.

The practice of using copper and constantan extension wires with chromel-alumel thermocouples is not recommended since it introduces errors too large to be ignored. Iron and cupronel as leads for chromel and alumel give a better match than copper and constantan and result in lower lead resistances than leads of the same size of chromel and alumel, as well as being less costly. But for best accuracy chromel-alumel thermocouples should be provided with chromel and alumel extension wires.

D. Color Coding

In making up the extension lead wires, either single or duplex, the insulating material is color-coded so that the proper combination will be used and that there will be no mistake such as connecting chromel lead wire to an alumel thermocouple wire. In every case the negative element has red in its covering.

E. Magnetic Check

As a hint for distinguishing between the bare thermocouple wires to which the extension wires are to be attached, it may be noted that the iron of an iron-constantan thermocouple is strongly magnetic and that the alumel of a chromel-alumel couple is perceptibly magnetic while constantan and chromel are non-magnetic. A small horseshoe magnet or a magnetized knife blade will serve to detect which of a pair is magnetic.

F. Insulation of Extension Wires

The insulating materials for extension wires are chosen with a view to durability in the surroundings to which they may be exposed. Enamel-covered wires and wire contained within a lead sheath are generally used where mois-

ture is present. Heat-resistant rubber is used where flexibility and high insulation are important. The rubber becomes hard and brittle when heated continuously to temperatures in excess of about 175 F. Organic insulating materials such as cotton, silk and wire enamel become brittle and eventually disintegrate when continuously exposed to temperatures in excess of about 250 F. Asbestos gradually decomposes at temperatures in excess of about 500 F. Glass fiber insulation disintegrates at temperatures in excess of about 1000 F.

The extension wires may fail due to over-heating not only at the head (where the temperature should never be in excess of 400 F) but also where they may traverse a hot region on their way to the instrument; for example, along a furnace wall or a steam line.

G. *Installation Precautions*

The installation of the wiring from the thermocouple to the measuring instrument should be carefully engineered. The leads should have a weather proof covering and should be run in metal conduits. The conduits should be grounded to prevent leakage from power lines or lighting circuits. Switches should have low and constant contact resistance and should be as free as possible of parasitic thermal emfs. If the instrument is to be used to measure the emf of more than one thermocouple, the extension wires of each thermocouple should be run, without interconnections, up to the switch at the measuring instrument. This switch should be of the double pole type, so as to keep the leads distinct all the way to the measuring instrument.

chapter 6

Measurement of thermocouple emf's

The basic fact of thermoelectric thermometry is that a thermocouple develops an emf which is a definite function of the difference in temperature of its hot and cold junctions. If the temperature of one junction is known, the temperature of the other junction can be determined by measuring the emf generated in the circuit. Measurement of temperatures with the aid of a thermocouple therefore requires the use of an instrument capable of measuring emf. In practice, two methods of measurement of emf are in use, the millivoltmeter and the potentiometer methods.

A. Millivoltmeters

The millivoltmeter consists of a galvanometer with a rigid pointer which moves over a scale graduated in millivolts or in degrees, F or C. The galvanometer indicates by its deflection the magnitude of the current passing through it, and if the circuit in which it is placed includes a thermocouple it measures the current, I, generated by the thermocouple in the circuit. If the circuit has a resistance, R, and the emf is E, by Ohm's Law, $E=RI$, and if R is kept constant E is proportional to I and the scale can be calibrated in terms of millivolts rather than in milliamperes or microamperes. This calibration holds good only as long as R remains constant. Any change in R introduces an error in the indicated value of E.

Changes in resistance may result from changes in temperature of the thermocouple or its extension wires or of the copper galvanometer coil; from corrosion of the thermocouple wires; from changes in the depth of immersion of the thermocouple; or from changes in contact resistance at switches or binding posts. Means are provided for adjusting the circuit resistance to a standard value, either manually or automatically. In order to reduce the errors resulting from such changes in circuit resistance it is common to increase the circuit resistance by inserting in the meter a resistance coil of manganin with practically zero temperature coefficient, so as to swamp out small accidental changes in circuit resistance. The added resistance may be 80 per cent of the total circuit resistance, reducing the value of I to one fifth of what it would have been without the added resistance and requiring a correspondingly more sensitive galvanometer.

The millivoltmeter is liable to change of calibration resulting from changes in strength of magnetic field and spring tension. Pivot friction introduces another source of error.

In spite of its limitations the millivoltmeter serves a very useful purpose in a

great variety of industrial measurements of temperature where the precision required does not demand the use of the potentiometer method of measurement. Its simplicity, and the fact that its temperature indication is as direct as that of other deflection instruments makes it attractive where a more expensive precise instrument cannot be justified.

B. Potentiometers

1. General Principles

Where precision is required in the measurement of thermal emfs, the potentiometer is invariably used. And because of its reliability and freedom from the uncertainties arising from changes in circuit resistance, meter calibration, etc., as well as its much greater openness of scale, it is used in many cases where the precision needed might not seem to justify the higher cost.

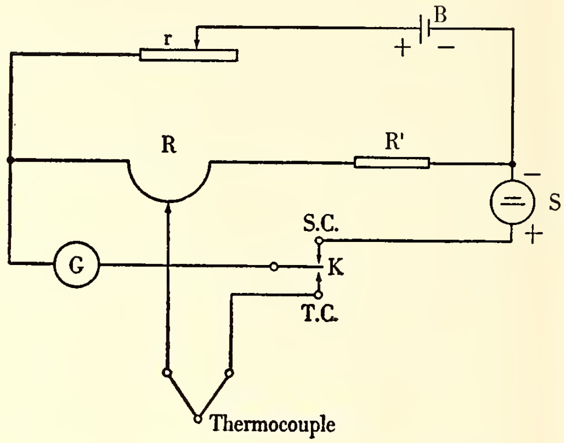


Fig. 19 Potentiometer Circuit, Schematic

Figure 19 shows a simple potentiometer circuit which includes a resistor R, a standard cell S, a dry cell or storage battery B, a galvanometer G, and a rheostat r. R may be a calibrated slidewire, with a known resistance, and R′ a fixed resistor such that R + R′ is some simple multiple of the emf of S. If e_s is taken as 1.019 volt the sum of R and R′ may be chosen as 101.9 ohms. If the switch K is turned to the standard cell position the galvanometer will, in general, deflect. The setting of rheostat r is adjusted until the galvanometer remains at rest when K is closed. Then the drop of potential of the battery current through R + R′ is exactly equal to the emf of S, so that if i is the current in R + R, $i = {}^{1.019}/_{101.9}$ ampere, or 10 milliamperes. Through each ohm of R there is then a drop of potential of 0.01 volt. If R is 20 ohms the total drop through the slidewire is 0.2 volt.

Now if K is turned to the "thermocouple" position a setting may be found for the sliding contact on R at which there will be no deflection of the galvanometer. At this position the drop of potential through R up to the contact is equal to the emf of the thermocouple. If balance occurs at the 5 ohm point, the emf of the thermocouple is $0.01 \times 5 = 0.05$ volt $=$ 50 millivolts.

In this measurement the galvanometer has been used only as a means of detecting the presence of a current and readings are made only when no per-

ceptible current is passing through it. Therefore, it is not calibrated, and it is only called upon to indicate unbalance with sufficient sensitivity to give the desired precision of setting of the sliding contact. An increase in the resistance of the thermocouple circuit can only increase the limits of positions of the contact between which there is no perceptible deflection, but does not affect the position of balance, nor the measured value of the emf. Since the galvanometer is used only to indicate the existence and direction of current, it is unnecessary to design it to give a linear relationship between current and deflection. Zero stability is not extremely important, since it is only necessary to look for departure from any equilibrium position when the key is closed to detect a need for adjustment and the direction in which it should be made. The galvanometer is usually of the suspension type, even in portable potentiometers, to avoid errors due to pivot friction.

Standard Cell

The standard of reference for all voltage measurements is the Weston standard cell, shown diagrammatically in Fig. 19-a. Two types are available, the saturated and the unsaturated.

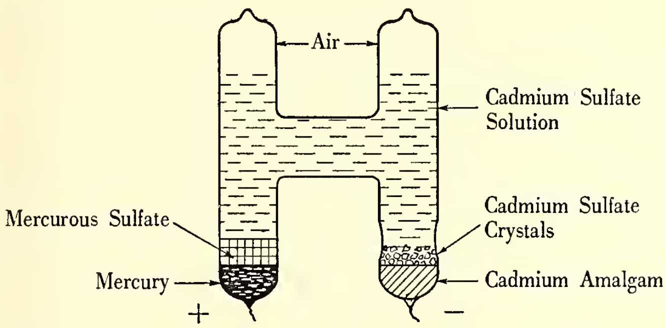


Fig. 19a. Diagram of the Weston saturated Standard Cell.

The saturated cell containing undissolved cadmium sulfate crystals is used in standardizing laboratories such as the National Bureau of Standards, to represent the value of the absolute volt. Its emf is 1.01864 absolute volts at 20 C, reproducible within a few microvolts and reasonably constant over long periods of time. From 10 to 40 C its temperature coefficient is negative, the emf decreasing by about 40 microvolts per degree C rise in temperature.

The unsaturated cell is the commercial form for potentiometric work. It is more portable than the saturated type, and its temperature coefficient is very near zero. When new, its emf is about 1.019 absolute volts. This tends to decrease about 100 microvolts (0.01%) per year, giving a useful life of about 10 years.

A standard cell must never be short-circuited, nor should its emf be measured with a voltmeter. In precise measurements, the balances should be made with a resistance of at least 10,000 ohms in series with the cell, until the balance is well within the range of the detector scale.

Ambient temperatures near the cell should remain between —4 C and +40 C if the cell emf is to remain within ±0.01% of its certified value. If permissible error is in the order of ±0.1%, these limits may be exceeded without

permanent damage. A standard cell packed in solid CO_2 will return nearly to its original emf within 24 hours of regaining room temperature.

Battery

A battery supplies the potentiometer circuit's current, and should be able to furnish 10 milliamperes for some hours with only gradual drop in emf. Either No. 6 dry cells or 40-80 amp-hr lead storage batteries may be used; the latter for more precise work.

To stabilize the discharge rate of either source during service, the circuit should be continuously closed through the potentiometer, even when the latter is not in use. Dry cells should be discarded and lead cells recharged before their voltages begin to drop too rapidly. Because both sources have appreciable temperature coefficients of emf, they should be protected against large or sudden temperature changes.

2. L&N Potentiometers for Use with Thermocouples

a. Manually Operated

Only a few of the many L&N potentiometers adapted for use in measuring the emf of thermocouples will be described, selecting some that are typical of the various degrees of precision that are available, going from the simplest to the more refined and complex circuits.

a1. Students' Potentiometer (L&N No. 7651)

The Students' Potentiometer is designed primarily as a laboratory instrument for teaching the student the principles of the potentiometer, but is also conveniently usable for routine measurements in an industrial laboratory where portability is not a requisite. To make it more instructive as an educational instrument only the various resistors of the potentiometer proper are enclosed in the potentiometer case. The user must connect up various component parts, such as standard cell, dry battery, rheostat, galvanometer, switches and keys, etc., in accordance with the diagram of Fig. 20. The permanently connected circuit elements are those shown diagrammatically within the dotted rectangle.

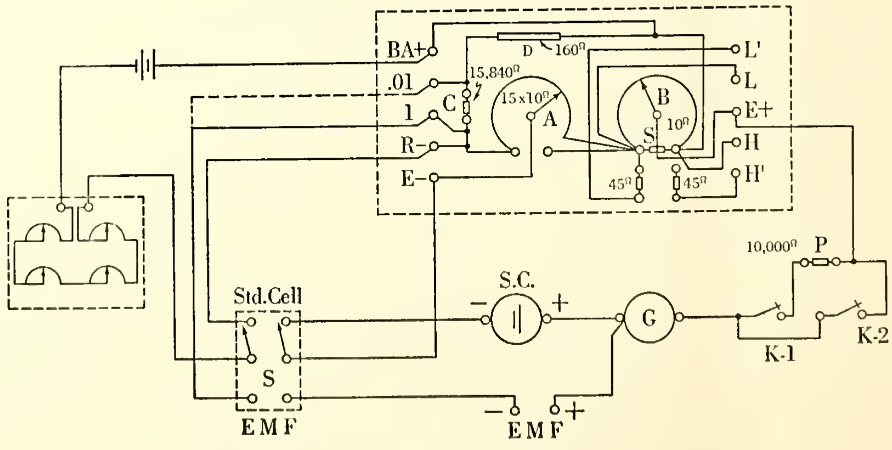


Fig. 20 Students' Potentiometer Circuit for Voltage Measurement

The dial switch indicated by A includes fifteen 10-ohm resistors while the slidewire B is shunted to a value of 10 ohms by means of the resistor S. The slidewire is about 12 inches long and on the disk supporting it is a scale divided into 100 main divisions, each corresponding to 0.1 ohm. The dial resistors, and the shunted slidewire are adjusted to equality within ± 0.04 per cent. In measuring an emf, contact is made on the various dial studs of A by the moving arm and on the slidewire B by a fixed contactor, past which the slidewire is turned. These contacts are in the galvanometer circuit and variations in their resistance do not affect the magnitude of the potentiometer current.

Current Adjustment

To adjust the current through the dial resistors and the slidewire to its required value, a standard cell with a known emf, for example 1.0190 volt, is put in series with a galvanometer and a tapping key, and connections are made at binding posts E— and E+ as shown in the figure. Dial switch A is set at 1.0 and slidewire disk B is set at 19.0. The resistance between the two contact points is then 101.90 ohms. Tapping the key K, the rheostat is adjusted until there is no observable deflection of the galvanometer when the key is closed. A more precise setting of the rheostat is made by proceeding with key K_2, making use of the full sensitivity of the galvanometer. Then the drop of potential in the battery circuit through 101.90 ohms is equal to the emf of the standard cell, 1.0190 volt and the current through A and B is 0.01 ampere. There is a drop of 10 millivolts through each ohm in these resistors. A displacement of one major division on the slidewire scale corresponds to 1.0 millivolt change in measured emf. Readings on this scale can be made to two tenths of a major division or to 0.2 millivolt.

Measurement of emf

To measure an unknown emf the double pole, double throw switch of Fig. 20 is put in the "EMF" position and the settings of dial A and slidewire B are adjusted until the galvanometer remains at rest when K_2 is closed. The unknown emf is then given in volts by the dial and slidewire settings.

Change of Range

Provision is made for changing the range so that instead of 1.0 millivolt per ohm in A and B the drop of potential is 0.01 millivolt per ohm, resulting in a range of 0 to 0.0116 volt. To accomplish this, the current through A and B is reduced to 0.0001 ampere. Connection is made to binding post ".01" instead of "1." Inspection of the figure shows that, when connected to "1," resistors C and D of values 15840 and 160 ohms respectively parallel A and B. Thus a resistance of 16,000 ohms parallels a resistance of 160 ohms, and the current through A and B is 100 times that through C and D. When the connection is made to ".01," C is in series with A and B, while D is in parallel with A, B, and C. Thus the current from the battery divides so that the current through A and B is reduced from its original value in the ratio of 100 to 1, while the battery current is unaffected. With the connections as shown in the figure, the standard cell balance is automatically made with 0.010 ampere in A and B even when the emf lead is connected to ".01."

External Components

Since the drop of potential through the measuring circuit must be 1.6 volt, the battery must have an emf in excess of this value. A single 2 volt storage

battery or two 1.5 volt dry cells in series are adequate for the purpose. The galvanometer should be chosen for adequate but not excessive voltage sensitivity. If measurements are to be made on the 1.6 volt range, it is customary to use a portable, pointer-type galvanometer with a sensitivity of about 300 microvolts per division. This is adequate since the slidewire reading cannot be made to closer than 200 μv and the galvanometer can detect an unbalance of 60 μv. When the 0.016 volt range is used, a more sensitive galvanometer should be provided, such as a box type lamp and scale galvanometer with a sensitivity of about 25 μv per scale division with which an unbalance of 5 μv can be detected.

The 10,000 ohm resistor P, introduced by key K, for reducing galvanometer current, need not be adjusted to a tolerance of less than ±10 per cent, but should be wire-wound, and of manganin to avoid parasitic emfs.

The double pole, double throw switch should be of a relatively thermal-free type, such as the pinch-type switch (L&N Cat. No. 3294). The battery rheostat is usually a four dial resistance box, adjustable in steps of 0.1 ohm up to 999.9 ohms (L&N Cat. No. 4715). Since the total circuit resistance is 200 or 300 ohms, depending on the battery used, 0.1 ohm steps make it possible to adjust the current to within 0.05 per cent of the required value. It is sometimes convenient to substitute for the dial of 0.1 ohm coils a continuously adjustable slidewire rheostat with a maximum setting of a little over one ohm.

Accessories and internal resistors and leads shown in the diagram which are not used in the measurement of thermoelectric emfs are not discussed here. The Students' Potentiometer has been described at some length as typical of several simple potentiometers.

a2. Double Range Potentiometer Indicator (L&N No. 8657-C)

This instrument is much used as a means of measuring thermocouple emfs in the laboratory or in the plant where spot temperatures are to be measured, recording instruments to be checked, etc. It is portable and self-contained, requiring only that the source of the emf to be measured be connected to the binding posts provided for the purpose, with due respect to polarity. It may be used with any type of thermocouple, for emfs from 0 to 64 mv. Its case contains dry cell, standard cell, galvanometer, switches and keys all properly connected for operation. To prepare it for use, the operator opens the lid, unclamps the galvanometer, sets its zero, standardizes the current and connects the thermocouple leads. To make a measurement he depresses the thermocouple key and turns the slidewire knob until the galvanometer pointer comes to zero. The emf is read from the slidewire scale. The circuit is fundamentally the same as for the Student Type Potentiometer. The current is standardized with the standard cell connected across a fixed resistance in the potentiometer circuit, the magnitude of which corresponds to the mean emf of the type of standard cell used. The probable difference in emf of standard cells from this mean is within the limits of error of the instrument.

Ranges

Since it is intended for use primarily for measurement of thermocouple emfs less than 64 mv the instrument is not provided with the dial switch in 10 mv steps and all readings are made on slidewire scale. On this scale there are two sets of graduations, 0 to 16 mv and 16 to 64 mv respectively, corresponding to

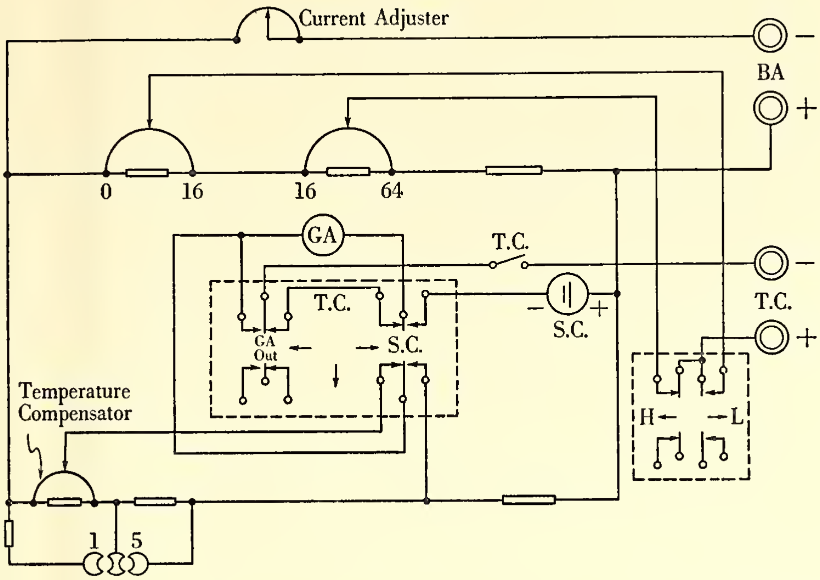


Fig. 21 Double Range Potentiometer Indicator Circuit

two slidewires mounted side by side on the slidewire disk and connected in series. To use the low range, the contact on the 0 to 16 mv slidewire is connected in series with the galvanometer, while for the high range the contact on the 16 to 64 mv slidewire is put in series with the galvanometer. The high range slidewire has three times the resistance of the low range slidewire, and there is the same drop of potential per ohm in each.

Reference Junction Compensator

This potentiometer includes a feature which is not present in the Student Potentiometer, namely, a manually adjusted reference junction compensator. (The methods of reference junction compensation will be discussed on pages 54-58.) In brief, the compensator enables the operator to set the instrument as required by the temperature at the thermocouple binding posts and the temperature-emf table for the particular thermocouple being used, so that the emf read on the main potentiometer dial is the same that the thermocouple would give if its reference junction were at the temperature of melting ice and the compensator were set at zero. This assumes that the thermocouple wires extend to the binding posts or that suitable extension wires connect the binding posts to the thermocouple head. The compensator must be set at zero if the potentiometer is to be used to measure emfs not resulting from thermocouples, or if it is to be used as a source of emfs for checking the accuracy of recorder or controller potentiometers.

For this latter purpose the galvanometer is shorted out by closing the appropriate switch to "Ga out," the dial is set to the desired voltage, and the leads from the instrument to be checked are connected to the thermocouple terminals. The potential to be supplied to this instrument is set up on the dial of the test instrument.

a3. Single or Double Range Indicator (L&N Nos. 8658, 8659)

This is a one-purpose potentiometer, similar in general appearance to the

preceding instrument but with its slidewire dial calibrated in terms of temperature, F or C, for a particular type of thermocouple—iron-constantan, chromel-alumel, copper-constantan or platinum-platinum 10 or 13 per cent rhodium and for a specified range or ranges. It is used to measure temperatures in laboratory or plant where continuous records are not needed, and to check the readings of permanently-installed instruments. The circuit differs from that of the preceding instrument in two important details. (a) It has an automatic reference-junction compensator instead of one of the manual type (See page 56). (b) In the two-range models the slidewires have independent scales on the same disk, one in red and the other in black. Each may cover any reasonable range of temperature and may even correspond to different thermocouple materials, such as iron-constantan on one scale and chromel-alumel on the other. This is accomplished by providing two independent circuits of equal total resistance, but different slidewire resistances, each with its automatic reference junction compensator. The currents in both circuits are standardized simultaneously when the balance is made against the standard cell.

a4. Portable Precision Potentiometer (L&N No. 8662)

The Portable Precision Potentiometer is a self-contained instrument having within its case all the elements needed to measure an emf connected across its "EMF" posts. It is designed to measure thermocouple emfs with a precision adequate for all but the more refined laboratory applications. It has within its

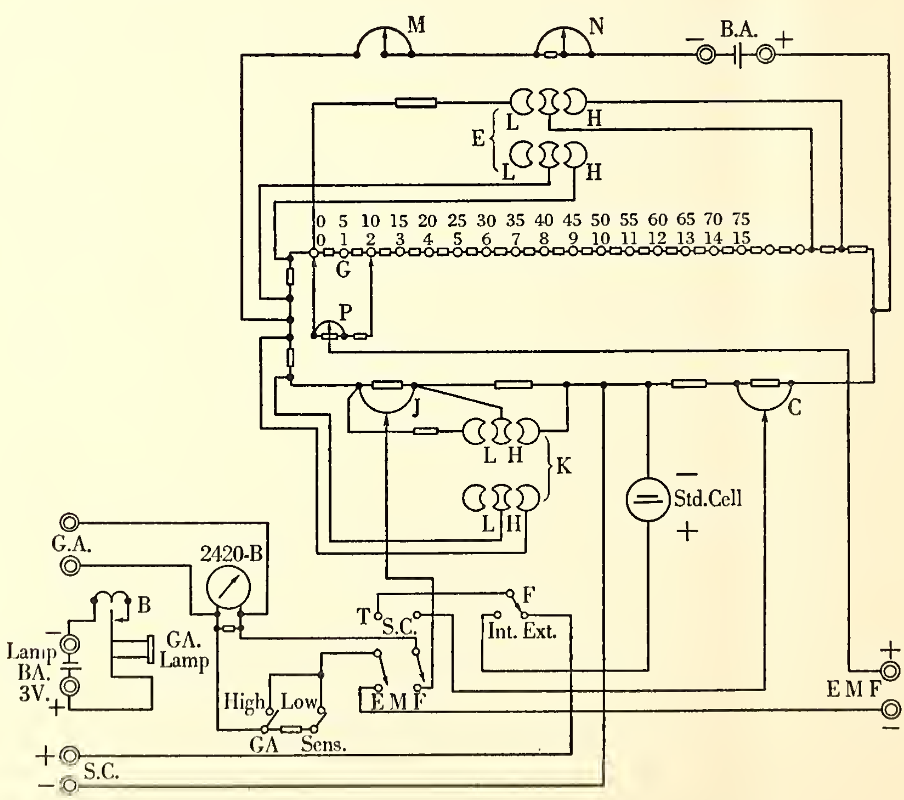


Fig. 22 Portable Precision Potentiometer Circuit

case a reflecting galvanometer which is more than ten times as sensitive as the pointer type galvanometer used in the potentiometer described above. This enables the user to work to narrower limits of error and requires that other parts of the circuit be held to correspondingly closer tolerances. For instance, instead of balancing the standard cell across a fixed resistance, one terminal of the cell is connected to a contact moving along a slidewire, which can be set so that the reading on a calibrated scale corresponds to the certified emf of the standard cell being used, if it is between 1.0166 and 1.0194 volt. This instrument has two ranges, 0 to 16 mv and 0 to 80.5 mv. As in the Students Potentiometer the calibrated portion of the circuit is made up of fifteen equal resistors connected into a dial switch, and of a slidewire which has a resistance that is 1.1 times the resistance of each of the dial resistors. The current is adjusted to such a value that there is a drop of potential of 5 mv in each resistor when using the high range and 1 mv when using the low range. Since the slidewire scale has 100 main divisions, readings can be made directly to 0.05 mv on the high range and 0.01 mv on the low range, with limits of error of ± 0.05 and ± 0.01 mv respectively. Two reference junction compensators are provided either of which can be used with both main ranges. One of these covers a range of 0 to 1 millivolt adjustable to 0.002 mv. The other has a range of 0 to 5 mv. adjustable to 0.01 mv. When the 0 to 5 mv compensator is used with the low main range, the limit of error becomes ± 0.02 mv instead of ± 0.01 mv. While it is primarily a portable laboratory instrument, this potentiometer may also be used in the plant for precise checking of installed thermocouples. The sensitive galvanometer is more affected by vibration and lack of leveling than the pointer-type galvanometer used in the other portable potentiometers. Consequently more care must be given to choice of location when the instrument is used for checking purposes in the plant than when a less sensitive instrument is used. The latter will give more reliable results than the more sensitive instrument in locations where there are severe vibrations, as in a power plant.

a5. Types K_1 and K_2 Potentiometer (L&N Nos. 7551 and 7552

The type K potentiometers are laboratory instruments for precise measurements of voltage. As applied to measurements of thermal emfs their characteristics are such as to make them the most generally used of all the potentiometers in this field, when accuracy and convenience of measurement are demanded. They are not portable in the sense in which the term is applied to the instruments just described, since to attain the results of which they are capable some parts of the circuit must be separately mounted. In particular when highest precision is required a very sensitive reflecting galvanometer with an all-copper circuit must be used, and this generally must be mounted on a vibration-free support. Dry cells are not sufficiently stable in emf, and storage batteries of at least 80 ampere-hour capacity are usually used as a source of constant working current. The standard cell is also external and mounted in its own case. It is provided with a certificate giving its emf at time of delivery to ± 0.01 per cent of the certified value. Being a separate unit, it can be sent from time to time to a certifying laboratory for re-checking. The inherent accuracy of the circuit elements in the potentiometer case justifies great care in selecting the accessory components.

Fig. 23 gives a schematic circuit diagram of the Type K-2 potentiometer. The Type K-1 potentiometer diagram differs from this in having only two

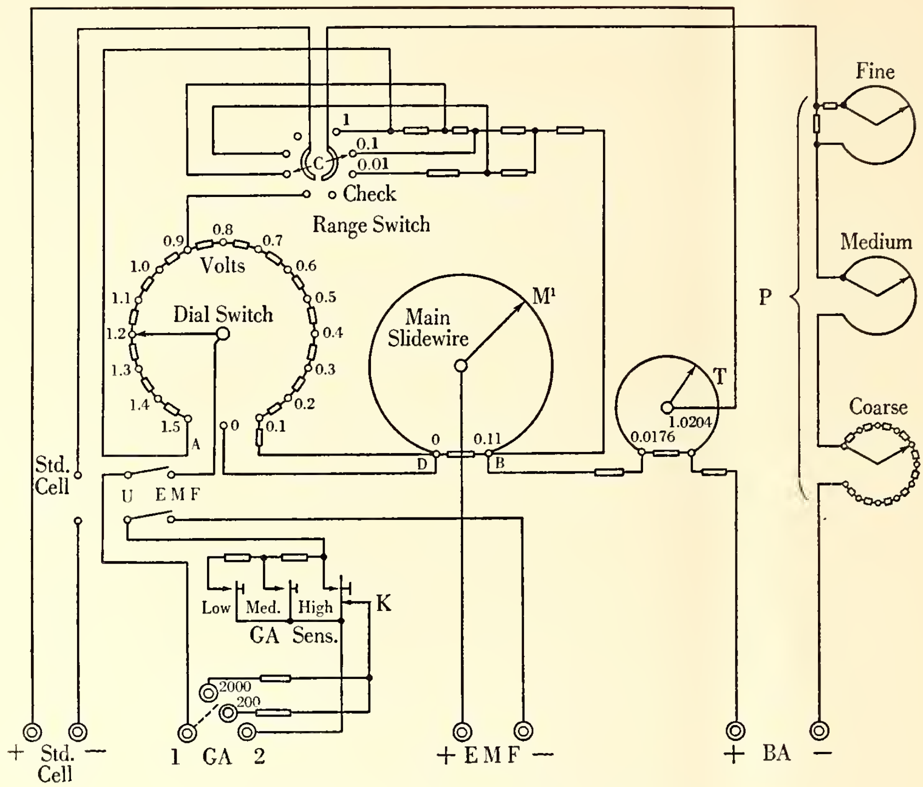


Fig. 23 Type K-2 Potentiometer Circuit
(Check Terminals and Connections not Shown)

ranges so that one point with its accompanying resistors is omitted from the range switch. The circuit is essentially the same as for the Students or the Portable Precision Potentiometer. The dial switch comprises fifteen resistors in series, each of which has a nominal resistance of 5 ohms. The absolute value of the resistance is of less importance than that the resistances of the individual coils shall be alike. They are adjusted to equality within a limit of error of ±0.01 per cent. Since they are from the same spool of manganin resistance wire and are identically wound and heat-treated, they maintain this equality very satisfactorily over a long period of years. The main slidewire, DB, consists of a uniform manganin wire, over five meters long, wound in a spiral groove of eleven turns on a bakelite cylinder fifteen centimeters in diameter. The bakelite cylinder is mounted rigidly on the top plate of the instrument. Contact is made with the slidewire by means of a hardened steel wire on a spring mounting, with the steel wire transverse to the slidewire, so as to make a point contact. A second spring close to the first carries a wiping pad instead of a contactor, serving to keep the slidewire clean. The two springs are mounted on a carrier which also supports a bakelite hood enclosing the cylinder, and which is threaded on a central stud so as to move up or down as the hood is turned, so that the contactor and wiping pad follow the convolutions of the slidewire. The angular position of the contact on the slidewire is indicated by a circular scale on the lower rim of the hood and the turn on which contact is being made is indicated by a vertical glass scale in front of the hood giving whole numbers of turns. A vertical line on this scale is the index for the angular

position of the contact. The scale on the rim of the hood has 200 graduations about 3 millimeters apart, so that the position of the contact can easily be estimated to one-thousandth of a single turn. Since each turn has a resistance of 0.5 ohm, settings can be made to 0.0005 ohm.

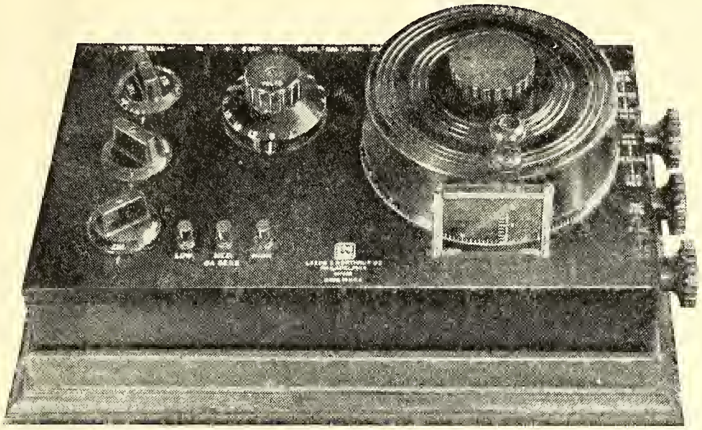


Fig. 24 Type K-2 Potentiometer

The slidewire is adjusted by means of a shunt coil to a total resistance 1.1 times the resistance of a single step on the dial switch or to nominally 5.5 ohms giving a resistance of 0.5 ohm for each of the eleven turns. The eleventh turn is provided to give an over-lap on the dial points so that when measuring an emf which may be fluctuating within limits, one of which is just below a certain dial value, and the other just above, it is not necessary to turn the dial one point and the drum through ten turns, to go from one limit to the other; for example, from 0.695 to 0.705. The slidewire is carefully uniformed in cross-section and is wound on the cylinder under constant, controlled tension, so that its resistance per unit length is constant throughout its length.

Ranges

The Type K-1 potentiometer is arranged to operate with working currents of either 5.0 or 0.5 milliampere in dial or slidewire coils, giving a range of 0 to 1.61 volt in one case and 0.161 volt in the other. The Type K-2 potentiometer has a third range of 0 to 0.0161 volt, with a working current of 0.05 milliampere. As in the case of the Students Potentiometer, the total battery current remains fixed when the range is changed, and when the current is standardized it is standardized for all ranges. The standardizing resistance is adjustable to correspond to the certified emf of the particular standard cell being used.

The range most frequently used for thermoelectric work is the intermediate or 0 to 0.161 volt range, which is readable to 1 microvolt. This is adequate for all but the most refined measurements such as those involving small temperature differences, or the calibration of thermocouples against platinum-platinum rhodium standard couples. The use of the 0 to 0.0161 volt range for these latter measurements should be subject to carefully observed precautions to avoid errors due to parasitic emfs. These may result from temperature

gradients in the slidewire caused by friction of the contactor and may be minimized by moving the drum very slowly as balance is approached and by allowing time for the heat developed by friction to dissipate before making a final setting or reading. Another possible source of spurious emfs is non-uniformity of temperature in the potentiometer such as might result from drafts or having one end of the instrument nearer to a radiator than the other. This is a consequence of the fact that there are various junctions of copper to manganin in the circuit and these may be at various temperatures, resulting in the generation of small emfs. Where it is desired to measure to fractions of a microvolt, it is preferable to use the Wenner potentiometer. (See page 52)

a6 White Potentiometers

The White potentiometers (single and double) were devised by Dr. W. P. White of the Geophysical Laboratories of the Carnegie Institution of Washington for use in measuring thermocouple emfs by a circuit which reduces the effect of parasitic emfs and which makes it possible to measure widely different emfs of two thermocouples with a minimum of dial adjustment and of delay.

Single Potentiometer (L&N No. 7620)

The White Single Potentiometer (Fig 25) has four resistance dials, making it possible to balance and read directly to four significant figures, the smallest step being 1 μv. The dials are used in pairs, designated as "upper" and "lower" respectively. The upper dials contain the larger steps, and are connected in

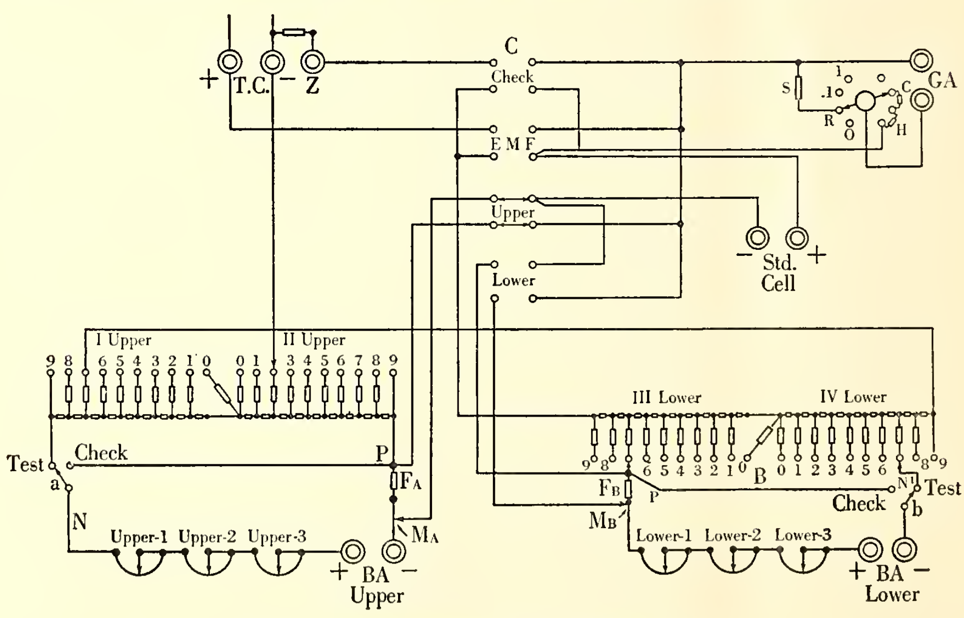


Fig. 25 White Single Potentiometer Circuit

series with a battery, rheostat and standardizing resistor, F_A. The contacts on these dials are potential terminals. Compensating resistors are provided to keep the resistance between the contacts constant for all settings on the two dials, so as to keep the resistance in series with the galvanometer constant. The lower dials have a separate battery, rheostat and standardizing resistor, F_B.

The contacts on these dials are current leads. Compensating resistors keep the resistance between contacts constant for all dial settings, so that the current remains constant while dial settings are changed. All the resistors of the lower dials are permanently in series with one of the potential contacts on the upper dials and the galvanometer so that to the difference of potential between the contacts on the upper dial, there is added the difference of potential between the contacts of the lower dials, due to the standardized current flowing through the resistors between them. The upper and lower dials are adjusted until the sum of the effects of the two sets is as nearly as possible equal to the emf of the thermocouple. The two higher dials make the coarse adjustments and are relatively infrequently adjusted so that the thermal emfs developed in them by friction are negligible. The lower dials have their contacts in the battery circuit rather than in the galvanometer circuit, and consequently any parasitic thermal emfs generated by the frequent operation of these dials are negligible in comparison with the battery voltage.

Since the resistance in the galvanometer circuit is kept constant by the compensating resistors, the galvanometer can be calibrated to give by its deflection the magnitude of any unbalanced emf, smaller than the least step of the lowest dial. A single standard cell and a single galvanometer are used, but the battery currents in the upper and lower dials must be standardized separately, and require separate storage cells. The advantages are almost complete elimination of parasitic thermal emfs such as are present when slide-wire contacts are used, and the ability to read to a fraction of the least dial step by observing the residual deflection of the galvanometer, resulting in more rapid operation.

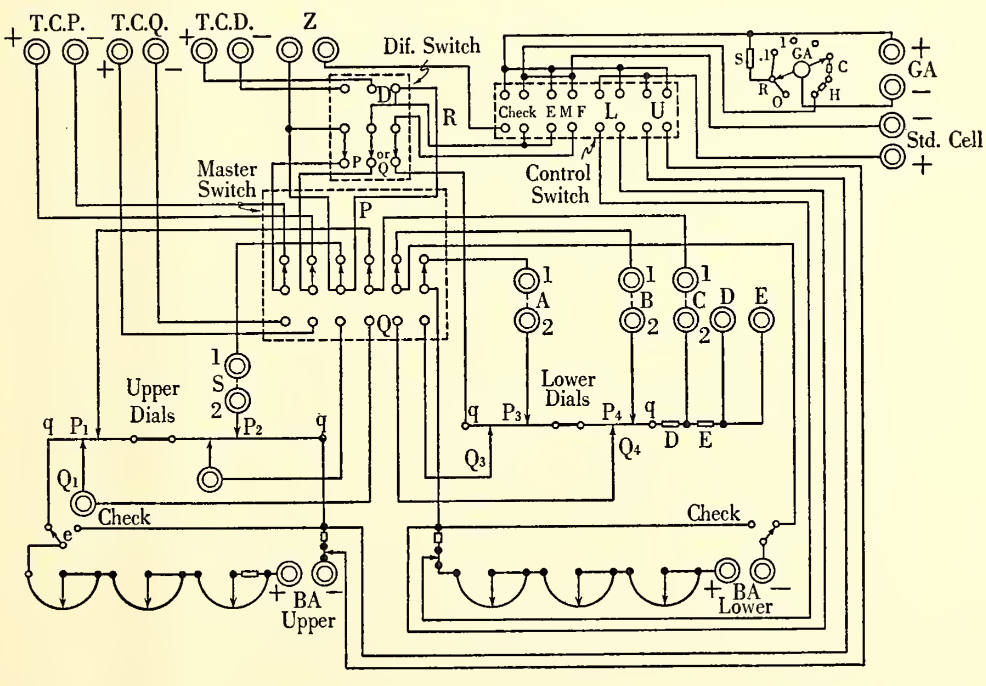


Fig. 26 White Double Potentiometer Circuit

Double Potentiometer (L&N No. 7622)

The White Double Potentiometer (Fig. 26) includes two such circuits as are described above, but with a single standard cell and galvanometer. The currents in the two sets of upper dials come from the same battery and are standardized simultaneously in one operation. The same is true for the two sets of lower dials. A master switch shifts the requisite connections from one potentiometer to the other. By this arrangement it is possible to make closely successive measurements on two thermocouples at widely differing temperatures by simply throwing the master switch from one side to the other. The dial settings for each of the thermocouples remain unchanged between readings so that only small adjustments need to be made to secure a balance. This is particularly useful in calorimetric work where two temperatures must be followed simultaneously. Provision is also made for measuring a small temperature difference with a difference thermocouple, using the galvanometer as a deflection instrument for measuring the difference emf.

a7 Wenner Potentiometer (L&N No. 7559)

The type of circuit used in the Wenner potentiometer (Fig. 27) was proposed by Dr. Frank Wenner of N.B.S. and the details of its construction were worked out at L&N in consultation with Dr. Wenner. It has some resemblance to the White single potentiometer in using moving contacts which are in the galvanometer circuit for the dials having the larger voltage steps, while the contacts of the lower dials are in the battery circuit. But the means employed for keeping the total current constant while varying the resistance through which the balancing potential drop takes place is quite different and is Dr. Wenner's chief contribution. It requires only one battery and a single current standardization instead of the two necessary for the White circuit. Suitable compensating resistors serve to keep the resistance in series with the galvanometer at a constant value of approximately 13 ohms. The low resistance of the important coils, and the way in which changes in these coils affect the measurement result in good stability, and also make it possible to use galvanometers with low critical damping resistance and high voltage sensitivity.

The contact resistance in any of the dials has an entirely inappreciable effect on the measurements. In the three lower dials the contacts are in series with resistances of a thousand ohms or more.

Electromotive forces that may originate during manipulation of the three lower dials have a negligible influence on the measured voltage, being in series with the battery voltage. Every precaution is taken to minimize parasitic emfs in the circuit. The temperature of the resistors is equalized by enclosing them in an aluminum chamber surrounded by bakelite. The resistors and the connections between them are all of manganin from the same melt, in order to reduce the chance of thermal emfs at junctions. Heat conduction is minimized by using small gage leads to all tap points. All terminals have copper circuits through them. The emf terminals to which the thermocouple leadwires are brought are inside the case, and are acessible through a small door.

With these and other precautions and with a suitably sensitive galvanometer, readings can be made over the high range (0 to 0.1111 volt) in steps of 1 μv with a limit of error of $\pm$ (0.01 per cent + 0.5 μv) and over the low range (0 to 0.01111 volt) in steps of 0.1 μv with a limit of error of $\pm$ (0.01 per cent + 0.1 μv). One microvolt corresponds to about 0.1 C when measuring temperature

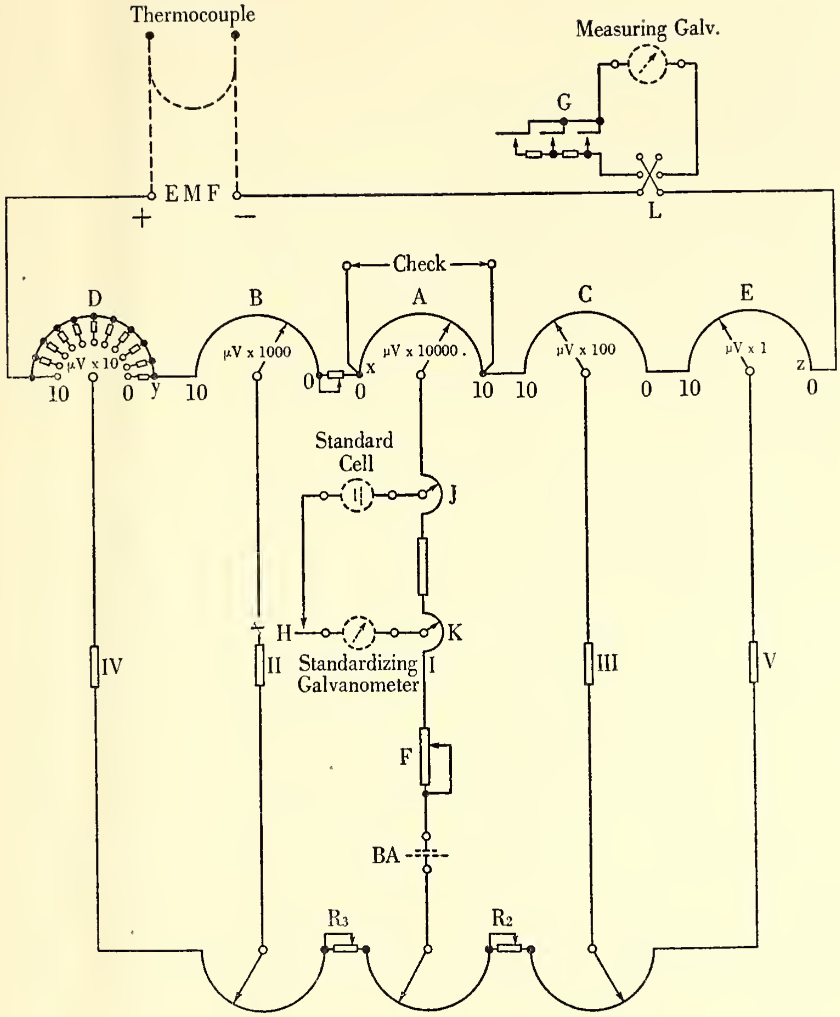


Fig. 27 Wenner Potentiometer Circuit
(Dotted Lines Indicate Accessory Apparatus)

with a platinum-platinum rhodium thermocouple.

The Wenner potentiometer is probably the most precise instrument now available for measuring thermal emfs. There is little present prospect of producing a more precise instrument.

The potentiometers which have been briefly described are only a few of those available, particularly in the field of portable instruments, but are chosen as being representative.

b. L&N Recording and Controlling Potentiometers

In discussing this subject no attempt will be made to describe recorder mechanisms except as some reference to operating details may be necessary to an understanding of circuit design. Fundamentally, the methods of recording and controlling temperature as measured with thermocouples are the same whether a Leeds mechanism, a Micromax, a Speedomax Type A or a Speedo-

max Type G recorder is used. In each case the circuit is a potentiometer not essentially different from the one used in the portable indicating potentiometers which have been described earlier. In practically every case automatic reference junction compensation is provided, and in the majority of the instruments provision is made for automatic current standardization against a standard cell, usually at 45 minute intervals.

Scales and charts are graduated in degrees, F or C, for a definite combination of thermocouple elements. In 1953, Leeds & Northrup lists 348 strip charts for thermocouples of which 227 are graduated in degrees F, and 121 in degrees C; and 119 round charts of which 74 are in degrees F and 45 in degrees C. Some of these are duplicates except for variations in time marking, some are arranged for use with two recording pens and some for three. Almost every reasonable requirement in the way of range to be covered and paper speed is provided for in these charts.

b1. Branched Circuit Potentiometer

In order that the recording potentiometer may record the actual temperature of the measuring junction of the thermocouple to which it is connected, without resorting to ice-baths or other means of maintaining the reference junctions at a constant temperature such as placing them underground in deep wells, means are provided for compensating for changes in reference junction temperature. The compensating device may be operated manually when a thermometer placed near the reference junctions indicates a change in temperature, or it may be made automatic.

b2. Manual Reference Junction Compensation

A method which has been much used for compensating for the fact that the reference junction is not in an ice bath or at some other fixed temperature is shown schematically in Fig. 28. The circuit resembles that shown in Fig. 19 but with the addition of a branch circuit, paralleling the potentiometer slidewire and its end coils. This branch consists of a slidewire D and a fixed resistor C.

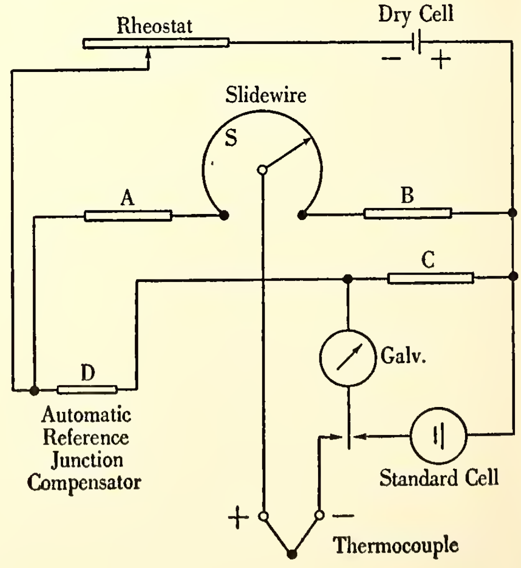


Fig. 28 Manual Reference Junction Compensation Circuit

The two branches of the circuit are made equal in resistance, so that when the rheostat is adjusted to make the current in one branch 5 ma, the current in the other branch is also 5 ma, and the battery supplies 10 ma. Resistor C is adjusted to such a value that the resistance of C plus a half of D is 203.9 ohms, so that when a current of 5 ma flows through this branch the drop of potential from the contact on D to the far end of C balances the emf of the standard cell within the required limits of error over a wide range of settings of the contact. The resistance of D may be 1 ohm, making the total resistance of this branch 204.4 ohms, so that the resistance of the other branch must also be adjusted to 204.4 ohms. The resistance of coil A is determined by the starting emf on the slidewire; the resistance of the slidewire is determined by the millivolt range to be covered by the slidewire; the resistance of the end coil B is adjusted to make the total resistance of the branch 204.4 ohms.

For example, a recorder for use with an iron-constantan thermocouple may be designed to record temperatures from 600 to 1600 F. For convenience in computation, using the Fahrenheit scale, the effective reference junction temperature will be assumed to be 0 F. Consulting the conversion table for iron-constantan with reference junction at 0 F, it is found that the emf of an iron-constantan thermocouple with its reference junction at 0 F is 18.08 mv, when the measuring junction is at 600 F and 50.92 mv when it is at 1600 F. For 600 F to fall at the low end of the slidewire, A must have a resistance of $\frac{18.08}{5}=3.616$ ohms. The potential drop through the slidewire, if its upper end is to fall at 1600 F must be $50.92-18.08=32.84$ mv, and its resistance must be $\frac{32.84}{5}=6.568$ ohms. It is adjusted to this value by shunting a nominally 20 ohm slidewire with a resistor such that their parallel resistance is 6.568 ohms. The resistance of end coil B must be adjusted so that $3.616+6.568+B=204.4$ ohms.

With the potentiometer circuit thus arranged and adjusted it is possible to read the true measuring junction temperature directly from the recorder scale even though the reference junction is at some temperature other than zero. Let the reference junction temperature be 75 F as measured by means of a thermometer placed near it. Using the circuit shown in Fig. 19 the recorder would balance at too low a temperature, since the emf generated by the thermocouple is less than it would be if the reference junction were at 0 F, by 2.16 mv, where 2.16 is the emf generated by an iron-constantan thermocouple with its reference junction at 0 F and its measuring junction at 75 F. This error could be compensated by adding 2.16 mv to the emf of the thermocouple. To accomplish this the thermocouple and galvanometer are bridged between the sliding contacts on the potentiometer slidewire and on D. The contact on D is set at such a point that the potential drop from the end nearer A to the contact is 2.16 mv. Then, since one thermocouple terminal has been displaced 2.16 mv along the lower branch, the slidewire contact must also be displaced 2.16 mv in the same direction along the upper branch to secure balance. Thus, the desired compensation is accomplished since, effectively, 2.16 mv has been added to the thermocouple voltage as read from the recorder scale.

The emf setting on D may be made with the aid of a scale associated with D, calibrated in millivolts, or preferably, if the recorder scale is direct reading in temperature for a particular type of thermocouple, in reference junction

temperature. Thus, in the case discussed above, the 2.16 mv point would be marked 75 F, and the other temperature markings would be in accordance with the emf-temperature curve for iron-constantan. With a 5 mv range for D, the highest reference junction temperature on its scale would be 173 F. The contact on D is set in accordance with the reading of a thermometer placed close to the reference junction, preferably in an enclosure which prevents rapid fluctuations in temperature. The enclosure may even be thermostated.

b3. Automatic Reference Junction Compensator

The manual reference junction compensator requires the personal attention of an operator to reset it whenever a significant change occurs in the reference junction temperature. To avoid the need for this personal supervision, practically all thermocouple recorders are provided with fully automatic reference junction compensators. Compensation is accomplished with the aid of a temperature-sensitive resistor which replaces the slidewire D of Fig. 28. The circuit is shown in Fig. 29. The galvanometer terminal which in Fig. 28 goes to the sliding contact on D is seen in Fig. 29, to be solidly attached to the junction point of D and C. Changes in potential drop through D are effected by

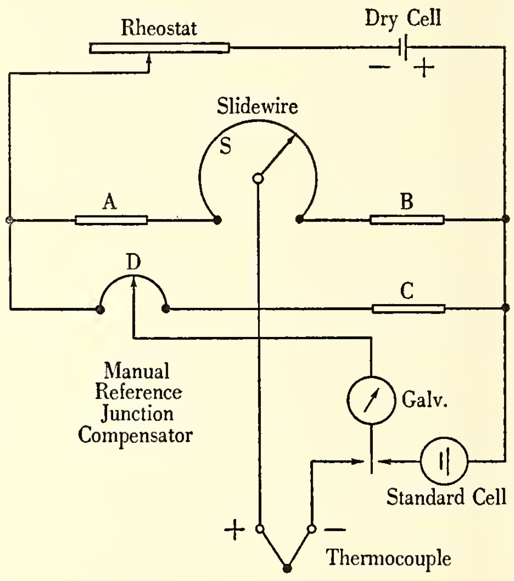


Fig. 29 Automatic Reference Junction Compensation Circuit

changes in its resistance resulting from changes in its temperature, rather than by changes in the position of a contact, and thus they move the position of balance of the contact on the potentiometer slidewire up or down scale in response to changes in the temperature of D.

The requirement for the resistor D is that over a limited range of temperature, such as 0 to 150 F, the rate of change of the drop of potential through it with change of temperature when the current is 5 ma shall be equal to the rate of change of the thermocouple emf over the same temperature interval at its reference junction.

If the recorder scale is to start at 0 F the end coil A must have a resistance equal to that of D when D is at 0 F. Then D must be so chosen that the drop in potential through it due to a current of 5 ma increases for a given rise in

temperature by the same amount that the emf of the thermocouple decreases for the same rise in temperature of its reference junction. If both the reference junction and the measuring junction are at zero, the recorder will balance at the zero end of its scale, since D and A are then equal. If the temperature of the reference junction and of D is kept at 0 F while that of the measuring junction is increased, the recorder will indicate the new measuring junction temperature correctly. If now the temperature of the reference junction is increased while D remains at zero, the recorder will indicate too low a temperature, since the thermocouple generates less emf because of the smaller difference of temperature of its junctions. If D is then brought up to the reference junction temperature and if it has the required resistance and temperature coefficient, the recorder will again indicate the true temperature since the contact must move farther up scale to balance the increased drop in potential through D.

To a first approximation the ratio of increase of emf and of resistance with increase in temperature may be considered as constant. Let R be the resistance of D at the reference junction temperature; K the change of resistance of D per ohm per degree; i the current flowing through D. Then Ki R is the increase in potential drop in D per ohm per degree increase in temperature. To secure compensation this should equal the thermoelectric power of the thermocouple at the same temperature. In the case of iron-constantan at 75 F this is of the order of 0.028 mv/deg. F. K, for nickel, is of the order of 0.0035 ohms/deg. F, also at 75 F. i is taken as 5 ma Then $R=\frac{C}{Ki}=\frac{0.028}{0.0023\times 5}=2.43$ ohms at 0 F. End coil A should also have a resistance of 2.43 ohms in order that the balance point may be at 0 F on the recorder scale when both the junctions of the thermocouple and also the resistor D are at 0 F.

The value of D as computed above is a rough approximation to the true value, and holds, even to this degree of approximation only at reference junction temperatures not very different from 75 F. It does not take into account the fact that neither the temperature-emf curve of iron against constantan, nor the temperature-resistance curve of the nickel of resistor D is linear in the range 0 to 150 F, over which compensation should be adequately precise.

The emf of the thermocouple with its reference junction at 0 F over this range is given by:

$$E=at+bt^2 \qquad (1)$$

while the resistance of D is given by:

$$R=R_0(1+a_1t+b_1t^2) \qquad (2)$$

The terms in b and b_1 in the above expressions determine the curvatures of the emf and the resistance curves, respectively. It is found by experiment that b_1 for nickel is larger than b for the iron-constantan thermocouple. To match the curvatures b_1 must be reduced. This can be accomplished by substituting copper for part of the nickel component of D, since for copper b_1 is practically zero from —50 to +300 F.

The proportion of copper resistance to be used can be computed precisely from the known values of a, b, a_1 for nickel, a_1 for copper, and b_1 for nickel (b_1 for copper is zero). It is found that for a current of 5 ma in each branch the resistance of the nickel component should be 0.6509 ohm and that of the copper 1.2434 ohm, both at 0 F. This provides almost perfect compensation

for reference junction temperatures, of an iron-constantan thermocouple up to 150 F.

For some thermocouples, a in eq. 1 is larger than a_1 for nickel. In this case constantan can be substituted for a portion of the nickel to reduce the a of the composite resistor to the desired value.

It will be noted that the compensation is fitted to only a single type of thermocouple, in this case iron-constantan. If a chromel-alumel or a platinum-platinum rhodium thermocouple is to be used, the values of R_0' and R_0'' must be computed to fit the values of a and b in Eq. 1, which are computed from their respective curves. If, to secure greater sensitivity, two or more thermocouples in series are used to measure the temperature, the resistance of D must be increased suitably.

Normal fluctuations in ambient temperature do not change the value of D sufficiently to affect the equality of the currents in the two branches of the potentiometer circuit appreciably. The standard cell balance always adjusts the current in the branch containing D and C to 5 ma. no matter what the value of D may be.

chapter 7

Standardization and calibration of thermocouples

The International Temperature Scale, adopted in 1927 by the Seventh General Conference of Weights and Measures, and reaffirmed, with very slight revisions, by the Conference in 1948, is fundamental to most precise temperature measurements. The scale is based upon a number of fixed and reproducible equilibrium temperatures (fixed points) to which numerical values are assigned, and upon specified formulas for the relations between temperature and the indications of the instruments calibrated at these fixed points. The numerical values assigned to the fundamental and fixed points as determined at the standard pressure of 1,013,250 dynes/cm^2 are given in the table below.

Primary Fixed Points

Materials	*Temp. C. (Int. 1948)*	
Liquid oxygen and its vapor (oxygen point)	*– 182.970*	
Ice and air saturated water (ice point)	*0.*	*Fundamental point*
Liquid water and its vapor (steam point)	*100.*	*Fundamental point*
Liquid sulfur and its vapor (sulfur point)	*444.600*	
Solid and liquid silver (silver point)	*960.8*	
Solid and liquid gold (gold point)	*1063.0*	

The ice and steam points are fundamental to the centigrade temperature scale and the values assigned to them are purely a matter of definition. The values assigned to the other (primary) fixed points were determined with the aid of constant volume gas thermometers and represent as closely as experimental methods have permitted, the temperatures of these fixed points on the thermodynamic scale. By the action of the International Council they are now defined values and in using them no reference need be made to the thermodynamic scale. The International Temperature Scale is defined in terms of these fixed points and interpolation procedures. The methods of definition chosen have been aimed to secure the best possible agreement with the experimentally determined thermodynamic scale.

In addition to the six fundamental and primary fixed points, various other well-determined fixed points are available. Some of these are given in the following table, the temperatures being based on the International Temperature Scale of 1948. Except for the triple points these values were determined under the pressure of 1 standard atmosphere.

Secondary Fixed Points

Materials	*Temp. C. (Int. 1948)*
Equilibrium between solid CO and its vapor	− 78.5
Freezing mercury	− 38.87
Equilibrium between ice, water and its vapor (triple point)	+ 0.0100
Triple point of benzoic acid	122.36
Equilibrium between naphthalene and its vapor	218.0
Freezing tin	231.9
Freezing cadmium	320.9
Freezing lead	327.3
Equilibrium between mercury and its vapor	356.58
Freezing zinc	419.5
Freezing antimony	630.5
Freezing aluminum	660.1
Freezing copper in a reducing atmosphere	1083
Freezing nickel	1453
Freezing cobalt	1492
Freezing palladium	1552
Freezing platinum	1760
Freezing rhodium	1960
Freezing iridium	2443
Melting tungsten	3380

A. Interpolation Between Fixed Points

While many means exist for comparing and measuring temperatures, only three methods are adopted by the Conference for use in determining temperatures between the primary fixed points which have been chosen. These are the platinum resistance thermometer from the oxygen point to the antimony point; the platinum-platinum 10 per cent rhodium thermocouple from the antimony point to the gold point; and the optical pyrometer from the gold point upward. Any other temperature measuring device is to be calibrated by more or less direct comparison with the one of these three which is appropriate for the temperature involved. Platinum was chosen as the material for use in resistance thermometers because of its stability, ductility, resistance to oxidation, availability in a highly pure state and absence of irregularities in its temperature vs. resistivity curve. This curve can be represented by a simple mathematical formula. The coefficients of the various terms in the formula are determined on the basis of measurements of the resistance of a particular platinum thermometer at the oxygen, ice, steam and sulfur points. The resistance corresponding to any other temperature within the range of these measurements, and beyond this range, as far as the antimony point, can be computed by substitution in the formula. The temperature scale thus established matches the Thermodynamic Temperature Scale within ±0.05 deg. C when the adopted values for the fixed points, as given in the table above, are used in computing the coefficients. It is the International Temperature Scale from the oxygen point to the antimony point.

Similarly, for much the same reasons, the platinum-platinum 10 per cent rhodium thermocouple was chosen as the means of reproducing in the laboratory the International Temperature Scale from the antimony point to

the gold point. The following is quoted from the text of the specifications for the International Temperature Scale of 1948 as given in the N.B.S. Journal of Research. Vol. 42, p. 211 (1949).

"From the freezing point of antimony to the gold point, the temperature t is defined by the formula

$$E=a+bt+ct^2$$

where E is the electromotive force of a standard thermocouple of platinum and platinum rhodium alloy when one junction is at 0 C and the other is at the temperature t. The constants, a, b, and c are to be calculated from measured values of E at the freezing point of antimony and at the silver and gold points. The antimony used in determining these constants shall be such that its freezing temperature, determined with a standard resistance thermometer, is not lower than 630.3 C. Alternatively the thermocouple may be calibrated by direct comparison with a standard resistance thermometer in a bath at any uniform temperature between 630.3 and 630.7 C. The platinum wire of the standard thermocouple shall be annealed, and of such purity that the ratio R_{100}/R_0 is greater than 0.3910. The alloy wire shall consist nominally of 90 per cent platinum and 10 per cent rhodium by weight. When one junction is at 0 C and the other at the freezing point of antimony (630.5 C), of silver, or of gold, the completed thermocouple shall have electromotive forces, in microvolts, such that

$$E_{Au}=10{,}300 \pm 50\ \mu v$$

$$E_{Au}-E_{Ag}=1185+0.158\ (E_{Au}-10{,}310)\ \pm 3\ \mu v$$

$$E_{Au}-E_{Sb}=4476+0.631\ (E_{Au}-10{,}310)\ \pm 5\ \mu v\text{"}$$

The determination of the coefficients a, b, and c in the quotation requires the use of melting point apparatus and very precise potentiometric measurements of the emfs developed by the thermocouple at the three standard temperatures. Then by substitution in the formula the emfs at any intermediate temperatures can be computed. It is customary to prepare a table of temperature against emf for the particular thermocouple, based on computations of E at fairly short temperature intervals. In general, such a calibration is best made at N.B.S. or other standardizing laboratories properly equipped for melting point determinations. The user will then base his temperature measurements with the thermocouple on the certificate issued by the laboratory. Such a certified thermocouple may be used as a reference standard of temperature in its range from the antimony to the gold point, and will commonly be used only for the purpose of checking working standard thermocouples, and not in routine measurements. It is more widely useful if it is also certified at a number of other fixed points between 0 C and the antimony point, and a table prepared in accordance with the procedure described under "Working Standard Platinum Thermocouple" (page 12), extending from 0 C up to about 1500 C. These fixed points may be selected from the list of fixed points in the table, or they may be bath temperatures, measured with a certified platinum resistance thermometer.

If the user desires to carry out the melting point determinations in his own laboratory he should use metals whose purity and melting points have been certified at N.B.S., since small traces of some impurities may change melting points significantly.

B. Calibration of Wires against Platinum

As illustrative of the methods generally used in the standardization of thermocouple materials, a method employed for the establishment of the temperature-emf relationship for an iron-constantan thermocouple will be described.

It will be assumed that a sample of No. 9 Birmingham gage iron wire and one of No. 8 B & S gage constantan wire are to be calibrated, to determine whether a thermocouple made up of these wires will match an accepted Iron-Constantan temperature-emf table within the required tolerances. It is not adequate to make up a thermocouple of the two wires and measure the emf at various temperatures, since this will give no clue as to which of the wires is at fault if the tolerances are exceeded.

The procedure followed for a precise check is as follows:

1. Preparation of Measuring Junctions

A sample of the iron wire, about three feet long, is cut off. One end of the specimen is flame-welded to a second iron wire from a tested roll of wire, so that the two wires lie side by side. A half an inch of wire from a spool of certified platinum is welded at one end to the bead at the junction of the two iron wires. To the exposed end of this wire is welded one end of a three-foot length of platinum wire from the same spool. This expedient is used in order to avoid shortening the long wire after each test, since the portion contaminated by the iron must be cut off and rejected before starting a new test. Welding the platinum to the iron bead assures that the junctions of iron to iron and of platinum to iron will be at the same temperature.

The junction of a working standard platinum thermocouple certified by N.B.S. at 100 C intervals up to 1000 C is placed with its junction touching the bead but not welded to it. The two iron wires are insulated with two-hole porcelain insulators over most of their length. The standard platinum wire is insulated with a one-piece, single-hole porcelain tube about 30 inches long, and the wires of the platinum-platinum 10 per cent rhodium thermocouple are enclosed in a one-piece, two-hole porcelain insulator, also about 30 inches long. Beyond these insulators, insulation is continued with fish spine insulators or glass beads, introducing colored glass beads at intervals for identification of the wires. The platinum thermocouple junction is sealed to the end of its tube with a mixture of sodium silicate and alundum, or with Pyrex glass, to protect it from contamination and to close the end of the insulator to prevent convection through it. The insulator for the single platinum wire is also sealed in the same way and for the same reason.

The collection of wires with their insulators is bound into a compact bundle with nichrome wire or other heat-resistant wrapping, avoiding any contact with the wires, and the welded junctions are placed in the furnace.

2. Reference Junction Procedure

Each of the external ends is inserted in a suitable copper block and held by means of a corrosion proof clamping screw. A block is provided for each wire, to each of which is soldered a rubber insulated copper leadwire tied to the block to prevent strain on the soldered joint. Each block is then immersed in a separate ice bath, consisting of a deep thermos jar filled with

crushed ice and water. The depth of immersion should be at least 4 inches for a No. 8 wire. This technique is very important when checking heavy wires. The cold junction technique usually employed with fine wires is to place each reference junction in a pool of mercury at the bottom of a glass tube, the insulated copper leadwire being placed in the tube with the thermocouple wire. The mercury forms the connection between the two wires. Several of these tubes can be placed in the same ice bath, since the glass tubes serve to insulate them from each other. The glass tubes should be kept clean and dry inside to avoid galvanic actions which might introduce parasitic emfs. This procedure is not satisfactory for No. 8 wires of relatively good heat-conducting materials. Glass is a poor conductor of heat, and heat conducted down the wire into the mercury may raise the temperature of the mercury appreciably above the ice point when equilibrium is reached between the in-flow of heat through the wires and the out-flow through the glass into the ice bath. Failure to recognize this source of error has introduced serious errors into otherwise precise calibrations of large thermocouple wires.

The spaces between ice particles must be filled with water (no air pockets) and the ice must extend all the way to the bottom of the container, water being drawn off with a syringe from time to time, and ice added and tamped down around the copper block and wires as needed. Left to itself a cavity may form around the wires as the conducted heat melts and in a dry atmosphere evaporates the ice around them, decreasing the effective depth of immersion. Commercially available ice, either artificial or lake, is satisfactory. Crushed ice cubes made from tap water in a domestic freezing unit can be used. The errors from the use of ice from such sources are not greater than 0.001 C and are negligible in these measurements.

The copper leads are connected to the measuring instruments through thermal-free selector switches.

3. Checking Furnace

The measuring junctions are placed in a furnace which must satisfy a number of requirements. Its temperature and its rate of change of temperature should be easily controllable over a considerable range. For the particular problem under discussion it should be possible to vary the temperature from 100 to 1000 C and to hold it nearly constant anywhere in this range for short lengths of time (in the order of 10 minutes). There should be a considerable zone of uniform temperature around the measuring junctions, and heat should be easily transferable from the furnace to the junctions, or vice versa. The depth of immersion of the junctions in the furnace is such as to assure that their temperature is not affected by temperature gradients along the wires.

A horizontal furnace which has been found satisfactory for the purpose is constructed as follows: The furnace heater consists of Nichrome* windings imbedded in a ceramic cylindrical shell, about 4 feet long and 4 inches in internal diameter, enclosed in a metal cylinder 15 inches in diameter and 4-1/3 feet long, with powdered silocel insulation between the heater and the metal walls and with the ends closed with preformed annular silocel bricks. A Nichrome tube 3¼ inches in inside diameter with a ⅛ inch wall and about 5 feet long extends through the bricks at each end forming a liner

** Nichrome is a trade name of Driver Harris Co.*

and heat distributor for the furnace winding. A metal cylinder 16 inches long and 2.5 inches in diameter is placed centrally to the length of the tube. It is bored to a depth of 15 inches, and an internal diameter of 1.5 inch, with the open end toward the open end of the furnace. Its material is aluminum bronze, which was chosen because of its resistance to oxidation and its fairly high heat conductivity. Copper cannot be used because of its rapid oxidation, though its high heat conductivity would otherwise make it preferable to aluminum bronze. The cylinder is fluted externally to facilitate its cooling by blowing air through the Nichrome tube. Exploration with a thermocouple shows that at equilibrium there is no perceptible temperature gradient along the central 10 inches of the cylinder.

A chromel-alumel thermocouple is inserted through the rear end of the Nichrome liner, with its measuring junction in contact with the end of the aluminum bronze cylinder and supported centrally by circular silocel bricks. It is connected to a recorder controller which records the approximate temperature, and shows the rate of change of temperature of the cylinder and also serves as a safety device to avoid accidental overheating. Rate of heating is controlled by auto-transformers, one of which is of the continuously variable or "Variac" type. Rate of cooling can be increased by blowing air through the Nichrome tube. The large heat capacity of the furnace, and its thorough heat insulation make its natural rate of cooling very slow, and also makes the temperature independent of short-period oscillations of line voltage. With practice in manipulating the controls in accordance with the indications of the recorder, the furnace temperature can be raised from 400 to 500 C and stabilized at 500 C in about an hour. "Stabilization" signifies reducing the rate of change of temperature to about a degree in five minutes as the desired temperature is approached. At lower temperatures such as 200 C more time is required to stabilize the temperature.

4. Measurement of emf

The comparison method used requires two precision potentiometers which are operated simultaneously. One of these may be a Type K potentiometer, but the other is of a type which does not use a slidewire for the fine balance, such as the Wenner. A sensitive, low-resistance, all-copper galvanometer is provided for each potentiometer. The two galvanometers are mounted side by side, and their spots of light are received on a single translucent scale, so that they can be observed simultaneously by a single observer. The type K potentiometer is used to measure the emf of the standard platinum couple.

5. Procedure for Comparison at a Fixed Temperature

The thermocouple junctions, prepared as specified above are inserted in the bronze cylinder in the furnace to such a depth that they are well within the uniform temperature zone, and the reference junction of each wire is placed in its individual ice bath, with its copper lead connected to the selector switch. The furnace is heated, first rapidly and then more slowly as the desired temperature, for example 500 C, is approached. The trend of the recorder curve will indicate to the experienced observer when to reduce the current, and how much, so as to pass through the 500 C point very slowly. The Type K potentiometer is set to balance the emf generated by the standard platinum thermocouple at 500 C, as given in the N.B.S. certificate, and its key is tapped from time to time to check the amount of

unbalance still existing. The Wenner potentiometer, measuring the emf of the thermocouple made up of the reference iron and the standard platinum wires, is adjusted from time to time to follow the rising emf of this thermocouple. When the temperature of the junctions is so close to 500 C that the Type K spot stays on scale when its maximum sensitivity key is closed, this key is locked down. The Wenner potentiometer is now kept in balance by adjusting its low voltage dial switches so that the hair line of its galvanometer spot is kept at its null position. The approach of the Type K spot to its null position is watched, and a final adjustment of the currents in both potentiometers against the standard cell is made about a minute before it is due to reach it. Just as the spot of the galvanometer corresponding to the standard thermocouple passes through its null position, indicating that the junctions are at 500 C, a particularly careful balance of the Wenner is made. The resulting setting gives the emf of the reference iron against standard platinum at 500 C.

Immediately thereafter the terminals of the iron under test and the reference iron are switched to the Wenner potentiometer by means of the selector switch, and the emf measured. This emf will generally be small, and may be either positive or negative, since the wires are of nominally similar materials, and differences between them may be in either direction. It is unnecessary to know the furnace temperature with a precision of better than ± 5 C in such a measurement, since the slopes of the temperature-emf curves of the two irons must be nearly identical, and a difference of a few degrees in furnace temperature would have no appreciable effect on the emf generated between them. It is therefore not necessary to measure the new furnace temperature by means of the Type K, if the irons are measured promptly after passage through the 500 C point.

We now have measured the emf of the reference iron against platinum at 500 C, and the emf of the reference iron against the unknown iron, also at 500 C. The algebraic sum of these emfs is the emf of the unknown iron against platinum at 500 C. This latter value could have been measured directly without bringing in the reference iron. The emf of the reference iron against platinum at 500 C is known from many previous measurements, and its measurement at this time serves as a check on the validity of the new value. If this departs appreciably from the established value it is an indication that there is something wrong with the measurement, requiring a careful check of the possible sources of error, and a repetition of the measurement. If the unknown iron were measured directly against the standard platinum, the value of emf obtained would have to be accepted, with no indication of the existence of disturbing factors. One possible source of error is non-homogeneity of the specimen of reference iron, which might not be discovered if the two irons were compared directly, without the check of the reference iron against platinum. The observations outlined above, repeated at various temperatures give (a) the temperature-emf curve of the specimen of reference iron against standard platinum; (b) the departures of the unknown iron from the reference iron; (c) the departures of the unknown iron from the ideal iron on which the standard iron-constantan tables are based. This last information results from the fact that the departures of the reference iron from the ideal iron are known and indicates whether the unknown iron is within the tolerances for thermocouple material.

The constantan wire is subjected to exactly the same tests, except that a reference constantan wire is used instead of the reference iron. Now having determined the emfs of the unknown iron and the unknown constantan against standard platinum at a number of known temperatures, by adding algebraically the emfs of the iron and the constantan at each of these temperatures, there results a very precise set of values for the emf of an iron-constantan thermocouple, made up of these two specimens.

This elaborate procedure is resorted to only when carrying out precise determinations, such as are required when measuring the effect of certain impurities, or purposely added components in the thermocouple materials. Readings are reproducible to closer than a microvolt when all the precautions are observed. Absolute accuracy will not in general be as good as reproducibility because of minor sources of error which are inherent in electrical circuits.

6. Calibration of Secondary Standard Thermocouples

The two specimens of iron and constantan which have been calibrated against platinum in accordance with the procedure in the preceding paragraphs may now be welded together at one end, and the bead of a working standard platinum-platinum rhodium thermocouple attached to the bead of the iron-constantan thermocouple, by welding, by insertion into a hole drilled in the base metal bead, or by binding it to the bead with a turn of platinum wire. The pair of junctions is inserted in the furnace and measurements of temperature and emf made by the two-potentiometer, two-galvanometer method. The values obtained at the various temperatures should agree with the summation of the values obtained for iron and constantan separately, against platinum. This is the more common method of calibration and is capable of very precise results. It is practically invariably used for the calibration of individual thermocouples intended for temperature measurements where accurate values are required. It is unnecessary to describe the process in detail, since it follows very closely that already described for simultaneous measurement of temperature and emf.

7. Calibration of Thermocouples at Low Temperatures

Thermocouples are extensively used in the measurement of temperatures in the range from —200 to +100 C. Copper-constantan thermocouples are generally used in this range, though iron-constantan thermocouples are also available. Calibration of thermocouples in this range is most readily accomplished by the use of fluid baths, at controlled temperatures, which are measured by means of standard platinum resistance thermometers. For temperatures above the ice point well stirred oil baths are usually employed, which may be supplied with both heating and cooling coils, and control devices for stabilizing the temperature at the desired values. So many of these control devices are available that it is hopeless to attempt to describe them or even to suggest which ones it is preferable to use.

For temperatures below the ice point, and down to about —70 C a thermally insulated alcohol bath can be cooled by means of solid CO_2, and held at a nearly constant temperature by adding bits of the solid CO_2 when an upward drift of the bath temperature is indicated by the resistance thermometer. The temperature of boiling oxygen can be attained with liquid oxygen in a Dewar flask; similarly liquid nitrogen or hydrogen can be used

for still lower temperatures.

Precautions must be taken in all these calibrations that the depth of immersion of the measuring junction is great enough to avoid heating or cooling of the junction by heat flow along the wires or their protection tube. The necessary depth of immersion is best determined by trial.

It is obvious that with the reference junction at the ice point the emf passes through zero at the ice point and reverses sign so that the leads to the measuring instrument must be reversed.

C. Acceptance Tests on Thermocouple Materials

The thermocouple materials, iron, constantan, chromel and alumel are carefully checked for departures from the accepted values for emf against platinum before being put in stock to be used in making up thermocouples. The check is made by comparing the sample with a reference wire of the same material, measuring the emf generated by a junction of the two wires when placed in a furnace at specified temperatures, usually 500, 1000, and 1500 F. The reference wires are chosen and standardized as follows:

A reel of No. 8 wire which, by checks on specimens taken from each end of the reel, is known to be good thermocouple material, is cut into three foot lengths. These, as they are cut, are laid out in ordcr, in groups of ten. All the members of the first group of ten are stamped with a numeral 1, the second group with 2, etc. The fifth member of each group is removed for calibration, as representative of the group. These test specimens are taken in lots of eight and one end of each is welded into a bead, together with an already calibrated specimen from an earlier lot of the same material, a platinum wire and a platinum-platinum rhodium thermocouple. The group of junctions is inserted in a furnace at the desired check temperature, to a depth of 13 inches, and left to soak for an hour. Checks are made on the stability of temperature by measuring the emf of the junction made up of the platinum wire and the wire from an earlier lot. A series of four or five readings are made, alternating with readings on the platinum-platinum rhodium thermocouple. When a steady state is reached, the emf of each of the eight new specimens against the reference specimen is measured ending with a repeat reading on the one first measured. The readings are made at 500, 1000 and 1500 F. If the spread of the measured emfs of all eight specimens against the reference is less than 10 μv, all the readings are averaged and the mean reading is taken as applying to all of them, and to the lots of ten which they represent. If one of the specimens is outside this limit, it is omitted from the average and its measured values ascribed to the nine which it represents. The test specimens are discarded, leaving nine of each lot for references wire, each of which will be used only once.

The reels of wire as received from the producer are coiled so that both ends are accessible. A three foot length is cut from each end of each reel and identifying marks stamped on the specimens removed and the reels are tagged with the same marks. The specimens thus prepared are welded together in groups of eight, together with one of the calibrated reference wires, and are placed in a furnace at 500 F, allowed to soak for an hour and the emf of each specimen against the reference wire is measured. This is re-

peated at 1000 and at 1500 F. On the basis of these measurements the reels represented by the samples tested are accepted or rejected. If the specimen from either end of a given reel is outside the permissible tolerances, the whole reel is rejected. A difference between the ends indicates inhomogeneity. Thermocouples made up of materials selected in accordance with this procedure will conform to the standard tables; for example, that for iron and constantan, or that for chromel and alumel, within ± 1.0 per cent of the measured emf at temperatures above 500 F and within ± 66 μv below 500 F, the wires being taken at random from stock, with no reference to their test data. Of course, by judicious selection very much smaller deviations can be attained. Even with random picking the probability of errors as large as those mentioned above is very slight, the probable error being not more than half of the possible error.

Tolerances for copper, and for constantan for copper are considerably narrower and the materials need to be checked only at relatively low temperatures such as are readily attainable in oil baths, the temperatures of which are measured with certified platinum resistance thermometers.

D. Calibration on a Production Basis

In addition to the large quantities of iron, constantan, chromel and alumel supplied to industry for applications where the tolerances of ± 1.0 per cent are more than satisfactory, there are many laboratory applications where much more accurate temperature measurements are required. To supply this need the Production Laboratory makes up many thermocouples of carefully selected materials, and calibrates the individual thermocouples, supplying the user with calibration data so that he can apply the corrections to the observed emfs to determine the true temperature or can prepare a temperature-emf table for the individual thermocouple.

1. Sub-Zero Calibration

From the oxygen point to 900 F (485 C) these special thermocouples are all calibrated by comparison with certified platinum resistance thermometers. At the oxygen point the junction is immersed in liquid oxygen in a deep vacuum flask, together with the platinum thermometer. A small flow of oxygen gas is kept bubbling through the liquid oxygen to produce stirring and to maintain uniformity of temperature. The temperature thus attained remains very satisfactorily steady. For a check point near —90 F (—70 C) the thermocouple and thermometer are immersed in a stirred alcohol bath, which is surrounded by a second bath of alcohol or acetone, to which solid CO_2 (dry ice) is added. This does not give a fixed point, but the temperature can be held reasonably constant by judicious adding of dry ice in accordance with the indications of the platinum resistance thermometer.

2. Oil Bath Calibration

At temperatures above the ice point and up to 500 F (260 C) well stirred and carefully controlled oil baths are used.

3. Calibration from 260 to 485 C

From 500 to 900 F (260 to 485 C) checks against the platinum thermometer are made by means of an aluminum block in an electrically heated thermally insulated furnace. The block is a cylinder of aluminum about 8

inches in diameter and 15 inches long placed in a vertical cylindrical furnace ("Hump" Type) of 10 inches internal diameter and 20 inch depth. The block rests on fire bricks at the bottom of the furnace. A sheet metal shell forms a screen between the heater and the block, touching neither of them. Heat is transmitted to the block mainly by convection. In the top of the block are drilled several 3/8 inch holes 12 inches deep, one central and the others in a circle, equally spaced from each other and equi-distant from the circumference of the block. The top is covered with a silocel brick pierced with holes corresponding with those in the block, which can be plugged with asbestos when not in use. A thermocouple recorder-controller is connected to an iron-constantan thermocouple with its measuring junction in the space between the heater and the shell. To operate at some temperature, such as 900 F, the control is set at 900 F and the current turned on in the heater. Because of the large heat capacity of the block and the location of the measuring junction the on and off action will start before the block reached 900 F, and the block will reach 900 F with little, if any, over-shoot. The current is reduced to such a value as to supply heat at a rate only little greater than the heat losses from the furnace. The current will then be on nearly all the time with brief off periods, and the temperature of the block fluctuates very little, and very slowly.

The temperature of the block is measured by means of a platinum resistance thermometer usually placed in the central hole. The thermocouples to be calibrated are placed in their protecting tubes in the other holes and readings made when their temperature is stabilized. Tests have shown that when stabilized the temperature difference between the central hole and any of the others is less than 0.01 C, and that the temperature of the block changes by not more than a degree per hour. It provides a very convenient and precise means of comparing thermometers and thermocouples in its range, from 500 to 900 F. It could be used at lower temperatures if oil baths were not available. The upper limit is set by the softening of aluminum above 1000 F. More refractory metals might be used for the block, but their thermal conductivity is not as high as that of aluminum. Copper oxidizes too rapidly to have an adequate life in service. If the cost is not prohibitive, silver is an excellent material for the purpose.

4. Calibration from 485 to 1000 C

For calibrations at temperatures above 900 F (485 C) electric furnaces are used, but without the equalizing blocks. The thermocouple to be checked has its measuring junction bound to the working standard platinum-platinum rhodium thermocouple with their beads in contact, or at least very close together. They are placed in a Fyrestan closed end tube and inserted in the furnace, which is brought up to the desired temperature and stabilized there. When stable, the emf readings on the two thermocouples are made. The upper limit of this calibrating furnace is about 2000 F, which is set by the properties of the heater coils.

5. Calibrations above 1000 C

To check a thermocouple, such as one of chromel-alumel, at higher temperatures use is made of an induction furnace. A well insulated hollow graphite cylinder is heated inductively by an a-c current with a frequency

of several thousand cycles. The thermocouple to be checked and a working standard platinum-platinum rhodium thermocouple, with their measuring junction beads touching are placed inside the heated graphite cylinder, allowed to stabilize and readings made with the heating current shut off, to avoid possible local heating of the thermocouples in the high frequency field. Checks can be made up to the upper limit of usefulness of the platinum thermocouple, about 2800 F (1540 C). A platinum wound furnace is very convenient for calibration purposes. Such a furnace can be used continuously at temperatures up to about 1200 C, but its life is seriously shortened if it is carried to much higher temperatures.

E. Checking Thermocouples in the Plant

1. General

The user of thermocouples can have confidence in their temperature indications only to the extent that he knows how closely the readings that he obtains conform to the actual temperature to be measured. Thermocouples are subject to deterioration particularly if used under unfavorable conditions. Process control cannot be carried out satisfactorily with thermocouples which are deteriorated or with instruments which are out of adjustment; therefore, thermocouples and their associated instruments should be checked from time to time, and thermocouples replaced or instruments adjusted or repaired when the checks show that there is need for it. The frequency of checking will depend upon the conditions surrounding the thermocouple and its equipment and will, in general, be dictated by experience. Some installations need no care for months, while others may need daily servicing.

2. "On the Spot" Checks

A very useful method of checking is the substitution of a reference thermocouple used only for checking purposes for the one in service and comparing their indications. This may be accomplished by removing the thermocouple under test from its well or protecting tube and replacing it with the reference thermocouple of the same type connected to a portable potentiometer which is known to read emfs correctly. If the temperature indicated is different from that given by the working thermocouple and its recorder or indicator, the difference may result from errors in either. The difficulty may be localized by replacing the working thermocouple in its tube, and measuring its emf with the portable potentiometer. If the reading agrees with that of the reference thermocouple, the trouble is to be sought in the measuring equipment or in the leads.

A method of checking which avoids interruption of the control of the process involves the installation of a blank protecting tube along side the one containing the thermocouple to be checked. The reference thermocouple is inserted in the blank tube and when temperature equilibrium is reached its emf is measured with a portable potentiometer. If a discrepancy is found it is localized by a procedure similar to that described above. If the operating temperature is above 1400 F (760 C), an optical pyrometer may be used to measure the temperature of the bottom of the blank tube, sighting through its open end.

The reference thermocouple must, itself, be standardized. Often the reference thermocouples are made up from certified wires, from spools or reels which have been selected by the supplier to give a particularly good match with the standard table. In plants which use many pyrometers it is common practice to standardize the checking equipment with precision standards maintained in the plant laboratory. Such laboratories usually maintain three platinum-platinum rhodium thermocouples for use as laboratory standards. One is used as a working standard for periodically checking plant reference thermocouples and two are held in reserve, for occasional comparison with the one in active use. If a comparison of the working standard with one of these shows a difference, comparison is made with the second of the reserve thermocouples to determine which of the first two is in error. The one which is in error may frequently be restored to usefulness by cleaning with borax, washing with alcohol, etc. (See page 21.)

The primary calibration of this laboratory standard is made most accurately by checking at the melting or freezing points of chemically pure metals. Because of technical difficulties this method of checking is not used in most industrial laboratories. Such checks are made at N.B.S., which will certify platinum-platinum rhodium thermocouples for a nominal fee to cover costs if they are to be used as laboratory standards.

3. Checking Furnace

Intercomparisons of plant standard and working standard thermocouples, and of working standards with the base metal reference thermocouples are usually made in a small electric furnace, having a zone of practically uniform temperature. Such a furnace is supplied as L&N Cat. No. 9003 or 9004. (Fig. 30). This consists of a cylindrical, Nichrome-wound heater, 4 inches

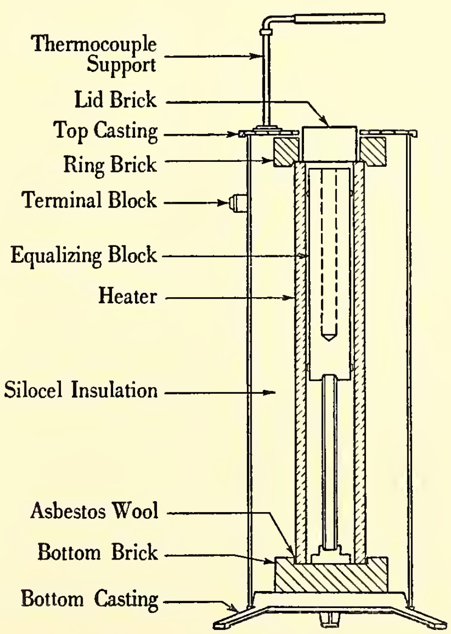


Fig. 30 Calibrating Furnace for Thermocouples

in inside diameter and 36 inches deep, closed at the lower end with a silocel brick. The metal casing is 14¼ inches in outside diameter, the space between the winding and the casing being filled with silocel in powder form to supply adequate heat insulation. The furnace has a continuous operation range from 300 to 1800 F with power inputs from 40 to 1000 watts. Power input may be increased to 5000 watts for rapid heating. It is a usual practice to heat the furnace to the highest temperature at which comparisons are to be made, and then by shutting off the power, to allow the furnace to cool through the desired temperature points. The cooling rate is slow because of the large heat capacity and the thorough thermal insulation, and comparisons can be made as it passes slowly through the various points. At the higher temperatures it is advisable to reduce, but not entirely cut off, the power so as to make the rate of cooling slow enough for good comparisons.

At the central portion of the working space the temperature stability and uniformity are consistent with industrial requirements for checking working standards. With the measuring junctions closely bound together and inserted at least 18 inches into the furnace, and the opening at the top plugged to reduce escape of hot air, checks can be made within ±3 F over the range from 300 to 1800 F.

To secure a uniformity and stability better than this, an equalizing block of copper is placed in the working space, supported on a pedestal. The block has a length of 20 inches and a diameter of 2¾ inches and has five longitudinal holes 18 inches deep bored in it. The thermocouples to be compared are placed in separate holes. Using the equalizing block, checks can be made within ±1 F from room temperature to 1000 F. Higher temperatures are not advisable since copper oxidizes too rapidly above 1000 F and the holes become blocked with scales of copper oxide. A similar block of aluminum bronze could be used at higher temperature, at least up to 1800 F, without serious oxidation. Uniformity would not be quite as good because of the lower thermal conductivity of the alloy, but is still much better than when no block is used.

4. Potentiometers Used in Calibration

When intercomparing laboratory standard thermocouples, the Type K2 potentiometer or its equivalent should be used, and in some cases the two-potentiometer method described earlier should be resorted to, where the results sought for justify it. The portable precision potentiometer (page 46) is amply adequate for intercomparison of base metal thermocouples with the working standards. The Type K is entirely satisfactory, though unnecessarily precise for the purpose. For on-the-spot checks the portable potentiometers with pointer-type galvanometers are adequate.

5. Inhomogeneity

Inhomogeneity in thermocouple wires is a frequent source of error and one which it is difficult to detect or to correct. By inhomogeneity is meant a variation in composition or in crystal structure along the length of the wire. It introduces errors only if it is in a region where there is a temperature gradient. It produces an additional emf in the circuit which may either aid or oppose the emf from the measuring junction. The precautions taken by the suppliers of thermocouple wires as described on pages 62 to 69 are

adequate to insure that no appreciable inhomogeneity is likely to be present in newly installed thermocouples. It develops during use when different parts of the wire are exposed to very different temperatures and atmospheres. Sharp inhomogeneities in a wire may be detected by connecting its ends to a galvanometer and moving a source of heat such as a bunsen flame or a hot soldering iron along it. A deflection of the galvanometer indicates the presence of inhomogeneity. Or the wire, connected to a galvanometer, may be doubled and inserted to varying depths in a checking furnace, so as to pass twice through a region of steep gradient. By moving the loop inward and outward, regions of inhomogeneity will cause a deflection of the galvanometer. Such tests give little information as to the magnitude of the error in temperature measurements introduced by the inhomogeneity. If it is a base metal wire, a positive test will usually serve as ground for discarding it. If it is a noble metal it may often be reconditioned by the procedure described on page 12.

chapter 8

Applications of thermocouples

A. General

The use of thermocouples is so general wherever temperatures are to be measured, recorded or controlled, that no pretense can be made that a complete listing of their applications is possible. It is not our aim to attempt such a task. We can only select some typical cases and indicate how thermocouples are used to secure the desired information. The field is so broad that it is difficult to choose, and we have a tendency to select the more unusual or difficult applications, and thus give an unwarranted impression that temperature measurement with thermocouples is a complex problem. On the other hand, a consideration of only the simplest cases might fail to impart an attitude of caution in accepting at face value the temperature indicated by a thermocouple.

B. Oil Bath Temperature

As a simple case we might consider the measurement of the temperature of oil which is well stirred in a glass container. Here the sources of error are at a minimum. The thermocouples, which may be of any of the accepted pairs of metals, can be inserted directly in the oil, without protective covering. The depth of immersion can be sufficient to entirely eliminate the possibility that the temperature of the measuring junction can differ from that of the oil because of heat flow along the wires. If the wires are fine, response is almost instantaneous. Since the oil is an insulator, there is no electrical leakage between the thermocouple wires and no electrolytic emfs are set up between them. The reference junctions can be placed in ice baths, with no extension leads between them and the measuring junction. The only uncertainties in the measurement are the calibration errors of the thermocouple and the errors which may exist in the measurement of emf.

C. Gas Temperatures

The situation is very different if the problem is to measure the temperature of gas in a duct through which it is flowing, and which is considerably hotter or cooler than the metal walls of the duct, as may occur in heating and ventilating, or in the flue gases escaping from a furnace. In the latter case the thermocouple will be inclosed in a metal protecting tube which is screwed into an opening in the wall of the duct. The inner surface of the metal wall is exposed to temperatures of 500 to 600 F while the outside temperature may be from 50 to 100 F. Therefore, there is a loss of heat

through the walls, and the inner surface is at a temperature considerably lower than that of the flue gas. The protecting tube then is cooler where it enters the wall than at its tip where the thermocouple junction is placed so that a flow of heat takes place through the tube and the thermocouple wires from the tip of the tube toward the wall. This heat must be supplied from the gas stream, and to pick up the heat the tube must be cooler than the gas. The temperature of the junction must, therefore, be lower than that of the gas. The magnitude of the resulting error will depend upon the heat transfer coefficient, which includes the rate of flow of the gas, the nature of the portion of the surface of the protecting tube exposed to the gas, the length, diameter and materials of the tube and the thermocouple wires, and the temperature of the wall to which the tube is attached. The errors are often of very significant magnitude. If the gas is cooler than the wall, the flow of heat will be in the opposite direction and the thermocouple junction will be at a temperature higher than that of the gas.

Or, suppose that a bare thermocouple, insulated with beads or refractory tubes is inserted through the wall. If the temperature of the flowing gas is stratified, the wires will pass through zones at different temperatures. If the wires pass through a cooler zone before reaching the junction, the junction will be at a lower temperature than that of the surrounding gas.

A further source of error is that resulting from radiation. In the case under consideration, of a hot gas inside cooler walls, there will be a loss of heat from the tube or thermocouple junction by radiation to the walls, in addition to that by conduction through tube and wires. Experience has shown that a thermocouple located in the hot gases, where it can "see" the cooler surfaces of the boiler wall may indicate temperatures 150 F too low when the actual gas temperature is 600 F. The radiation error decreases as the area of the radiating surface of the junction or tube is decreased. Consequently, this area should be made as small as is consistent with mechanical strength. The errors from conduction and radiation can be decreased by inducing a high velocity of flow past the sensitive element. This increases the convective transfer of heat to the element by providing a greater volume of hot gas, and also by stripping off the stagnant layer of adsorbed gas clinging to the thermocouple and forming a heat insulating covering. This is the principle of the suction or aspiration pyrometer. The radiation errors may be reduced by enclosing the sensitive element in a radiation shield, which may consist of two or more concentric cylinders, of materials of low emissivity, which prevent the sensitive element from "seeing" any cooler surface, but permit a free circulation of gas. The radiation error may be eliminated if the shields are provided with independent sources of heat and each is provided with a thermocouple. By adjusting the auxiliary heating the thermocouples may all be made to read alike, and there can then be no loss of heat by radiation or otherwise between the shields or between shield and sensitive element.

If the purpose of the measurement of the temperature of the gas is to work out a "heat balance" in a test of the efficiency of a power plant it is not sufficient to measure the temperature at one point in the gas, since the flow is invariably more or less stratified. It is not sufficient to measure the temperature simultaneously at a number of points since the velocity of

flow and consequently the mass of gas represented by each measurement is variable from point to point. It is necessary, by careful testing, to evaluate the rate of flow at the various points and to weight the temperature readings according to the flow. And this distribution of gas velocities is subject to change with each change of boiler rating.

This particular problem has been discussed at some length as representative of the difficulties that may be encountered in the measurement of temperature with thermocouples. It is fortunate that few thermocouple applications offer as many sources of error, or as difficult to compensate. The discussion is abstracted from the A.S.M.E. Power Test Code, Instruments and Apparatus, Part 3, Temperature Measurements.

D. *Power Plant*

In the power plant there are many other applications for thermocouples in addition to flue gas temperatures. Some of these are the temperatures of pulverized fuel, combustion air, superheated steam, throttle temperature, bled steam, and bearing temperature. All of these are continuously measured and recorded, and some are automatically controlled.

E. *Metallurgical*

The science of metallurgy is very dependent on the thermocouple as a tool for research and for carrying the results of research into industry. The metallurgists furnished much of the incentive for the advancement of the art of thermocouple pyrometry. It is of use to them in smelting, refining and casting of non-ferrous metals; in blast furnace iron smelting; in open hearth steel production; in brazing and welding, in soaking pits, forging mills, rolling mills, tin plating and galvanizing, hardening, tempering carburizing, nitriding, annealing and normalizing, etc. In the laboratory the metallurgist uses the thermocouple in a multiplicity of ways for research, testing and inspection.

F. *Ceramics*

The ceramic industry, in which we may include cement, porcelain and pottery, brick and tile, glass, etc. uses the thermocouple in the control of kiln temperatures, mold temperatures, lehrs, fuel, etc.

G. *Chemical*

The chemical industry uses great numbers of thermocouples in an enormous variety of applications, from the lowest to the highest temperatures. One of the outstanding chemical applications is in the refining and cracking of crude oil. Others are in electroplating, filtering, precipitating, distilling, evaporating, burning and calcining.

H. *Food*

In the food industry thermocouples are used in refrigerating and freezing, in baking and drying, in preserving and purifying, as well as in shipping and storage.

It is hopeless to attempt to list the applications of thermocouples in instructional, research and development laboratories in every branch of science. They may measure the body temperature of infant rats, or the cooling rate of the concrete work of the Hoover Dam, where thousands of feet of thermocouple wires were imbedded for this purpose.

I. General Precautions

It is impossible to give instructions for the use of thermocouples, except in the most general terms. Each application presents its own particular problems, either of installation, of maintenance or of measurement of emf. One principle that is common to all applications is that the thermocouple measures only the difference of temperature between its measuring and its reference junctions and unless the measuring junction is actually at the temperature of the body or region in which we are interested, its indications are in error. Another is that the temperature measurements are no more precise than the match of the particular thermocouple used with the temperature-emf relation which it is assumed to follow. Thermocouples should be made up of wires which have been carefully tested for match with the accepted calibration curve and for stability under operating conditions, and should be checked at suitable intervals.

If a permanent thermocouple installation is to be made in a plant, the lay-out of the equipment and the details of wiring, switches, panels, and recording and controlling instruments should receive careful attention. Leadwires should be run in grounded metal conduits. The leadwires themselves should have weatherproof heat resistant insulating coverings. All joints, except at the thermocouple head should be soldered and taped. Selector switches, where more than one thermocouple is to be connected to a measuring instrument, should be of a double pole variety, so that both leads of a thermocouple are disconnected from the measuring circuit when transferring to another thermocouple. It is not good practice to use a common lead to a group of thermocouples. The leads should not be run through hot regions; for example, over poorly insulated furnaces where they may be exposed to temperatures high enough to injure their insulation. Recorders or indicators should be suitably protected from weather, and from factory fumes and dust, and should not be mounted in such a way as to be subject to severe shock or vibration. They should be accessible and easily visible in order to give their best service. Since potentiometric instruments contain standard cells they should not be subjected to temperatures much below freezing, or above 50 C, which may ruin the cell. In the case of electronic recorders an attempt should be made to reduce to a minimum all loops in the electric circuit which might pick up stray a-c fields, and result in erroneous recording.

chapter 9

Limitations of thermocouples

In spite of the versatility of thermocouples, there are applications for which they are not well suited and in which other temperature measuring devices are preferable. They seldom displace the purely indicating thermometers which are based on expansion, such as the liquid-in-glass, or the bimetallic strip thermometers, for direct, non-recording observation of temperature in accessible locations. The simplicity of the expansion thermometers and their low cost make their use almost obligatory in a great many fields. But, in the very large areas of measurement where temperatures are to be recorded as well as measured, or if the readings must be made at a distance, or if the location where the temperature to be measured is inaccessible to the bulb of a thermometer, the thermocouple very often replaces the mercury thermometer. In this low temperature range a choice is often to be made between the use of a resistance thermometer or a thermocouple. The thermocouple has the advantage in speed of response, in bulk, and in cost. The resistance thermometer has greater potential sensitivity, making it possible to measure to a smaller fraction of a degree. It does not require a fixed reference junction. It may be operated on a-c, eliminating all need for batteries. Recorders and indicators can be provided with much narrower temperature ranges than for the thermocouple. The two electrical methods of measuring temperature are definitely competitive over the range of temperature from —200 to +500 C.

In choosing between them the user needs to study the requirements of his application, and determine which method offers most advantages.

For example, in the measurement and recording of atmospheric temperature the U. S. Weather Bureau makes use of the resistance thermometer for precise measurements. The choice is made on the basis of sensitivity over a relatively narrow range of temperature, freedom from reference junction errors, and simplicity of operation due to the fact that a Wheatstone bridge requires no standard cell and no standardization of battery current.

To measure subcutaneous temperatures of the human body the research worker makes use of a thermocouple. The thermocouple junction can be inserted, like the point of a hypodermic needle, under the skin and measure the temperature there. A resistance thermometer cannot be made small enough for the purpose. The experimenter would use either a mercury or a resistance thermometer for measuring arm-pit or rectal temperatures.

In the range of temperatures above 500 C the radiation pyrometer is

competitive with the thermocouple and above 750 C the optical pyrometer also is competitive. Both use potentiometric measuring apparatus. The radiation pyrometer is capable of recording and controlling while the optical pyrometer can only indicate. They may replace the thermocouple where temperatures are too high, where atmospheres cause deterioration of thermocouples, where moving bodies are involved, where high speed of response is required, etc. Radiation pyrometers are initially more costly and are subject to errors due both to uncertainty as to the emissivity of the source and to absorption of radiation by media in its path. It is sometimes difficult to secure an unobstructed view of the portion of the source which is to be measured. Offsetting the high initial cost is the low cost of maintenance since the radiation pyrometer is not deteriorated by the high temperatures that it measures.

chapter 10

Trouble shooting

The thermocouple, particularly when used in industrial processes, is subject to hazards which may affect its accuracy, put it temporarily out of operation or even destroy it. Its measuring or recording instrument is also subject to failure or inaccuracy. The user should be prepared to diagnose troubles as they may arise, and to take steps to correct them. Simple directions accompany most of the instruments which will aid in locating the source of trouble and give the steps to be taken to correct it. A few of the situations which may arise are as follows:

(1) The instrument does not respond to change in temperature. This may result from:

a. A broken or burned out thermocouple. To be discovered by removing the thermocouple from its protecting tube for examination or by applying a voltage to it at the binding posts in the head after disconnecting the extension leads and observing the current that flows through it, if any. If there is no current, the thermocouple is burned out or broken. If there is an intermittent or fluctuating current, there is a loose connection or an incipient breakage.

b. A faulty selector switch if a multipoint recorder or indicator is being used. To be detected by connecting the thermocouple leads directly to the measuring circuit, by-passing the selector switch.

c. A short-circuit, which may exist in the terminal head or in the extension leads, or even inside the thermocouple protecting tube. To be detected by checking for current from an applied voltage when the circuit is nominally open. That is, "ring out" the circuit.

(2) Instrument Reading is Erratic

If the indication of the measuring instrument fluctuates when the thermocouple is known to be exposed to steady temperature conditions, the cause may be:

a. A loose connection at binding posts, or a poor contact with the instrument slidewire, or a broken wire, either in thermocouple, leads or elsewhere, which intermittently breaks the circuit. To be located by pulling or shaking leads, inspecting binding post connections and the thermocouple itself.

b. Poor contacts in the selector switch due to dirt, corrosion or wear. Clean the contact points, and apply a thin coating of petrolatum. Tighten screws, and look for loose parts.

c. Faults in the measuring instrument, such as poor contact, loose connections or obstruction to free movement of the galvanometer pointer. Such faults often require the attention of a trained service man.

(3) Instrument Reads Low, or High

a. Galvanometer zero may need adjustment.

b. Cold junction compensator (if manual) may not be set correctly.

c. The battery current in the potentiometer circuit may need standardizing.

d. The thermocouple may have deteriorated by contamination or oxidation. Substitute a new thermocouple.

e. The extension lead wires may be reversed at the thermocouple head. Apply necessary tests, and consult color code to assure that the lead wires are properly connected.

f. The leads from the thermocouple may be reversed at the measuring instrument.

g. A chromel-alumel thermocouple may have been accidentally connected to an instrument calibrated for an iron-constantan thermocouple, or vice versa.

h. There may be a high resistance leakage path between thermocouple wires or lead wires so that the drop of potential through this high resistance rather than the total emf of the thermocouple is being measured. Disconnect the lead wires at both ends and measure the resistance between them. If the resistance is not sensibly infinite; i.e., of the order of a megohm or more, the leads and head should be inspected for damp spots, residual soldering flux, etc.

i. The measuring instrument may have changed in calibration. Check it with a portable potentiometer.

j. A high reading may result from a deteriorated standard cell. The voltage of the standard cell may be checked with a potentiometer (*not* with a voltmeter), or a new standard cell may be tried. Under no conditions should the standard cell be shorted.

Relationships of EMF & Temperatures for 4 Widely-Used Thermocouples

Electromotive Force vs. Temperature

Thermocouples

Copper vs. Constantan (Degrees Centigrade)	*Platinum vs. Plat. + 10% Rhodium* (Degrees Centigrade)	*Chromel vs. Alumel* (Degrees Centigrade)	*Iron vs. Constantan* (Degrees Centigrade)	*EMF in Absolute mv.*	*Iron vs. Constantan* (Degrees Fahrenheit)	*Chromel vs. Alumel* (Degrees Fahrenheit)	*Platinum vs. Plat. + 10% Rhodium* (Degrees Fahrenheit)	*Copper vs. Constantan* (Degrees Fahrenheit)
			–166	–7	–267			
			–136	–6	–212			
–169		–158	–109	–5	–165	–253		–272
–124		–118	–85	–4	–121	–180		–192
–88		–84	–62	–3	–80	–119		–126
–56		–54	–41	–2	–42	–65		–69
–27		–26	–20	–1	–4	–15		–16
0	0	0	0	0	32	32	32	32
25	147	25	20	1	67	77	296	78
49	265	49	39	2	102	121	509	120
72	374	74	58	3	136	165	704	162
94	478	98	77	4	170	208	892	201
115	578	122	95	5	203	251	1072	240
136	675	147	113	6	236	296	1247	277
156	770	172	132	7	269	341	1417	313
175	861	197	150	8	302	386	1582	348
195	950	222	168	9	334	431	1742	382
213	1037	246	186	10	367	475	1899	416
232	1122	271	204	11	399	519	2051	449
250	1205	295	222	12	431	563	2202	482
268	1288	319	240	13	464	606	2351	514
285	1372	343	258	14	496	649	2501	445
302	1456	367	276	15	529	692	2652	576
319	1540	391	294	16	561	735	2803	607
336	1624	414	312	17	594	778	2955	637
353	1709	438	330	18	627	820	3109	667
370		461	348	19	659	862		697
386		485	366	20	692	905		726
		508	385	21	724	947		
		532	403	22	757	989		

Temperature vs. Electromotive Force

Thermocouples

Copper vs. Constantan (Absolute Millivolts Centigrade Scale)	*Platinum vs. Plat. + 10% Rhodium* (Absolute Millivolts Centigrade Scale)	*Chromel vs. Alumel* (Absolute Millivolts Centigrade Scale)	*Iron vs. Constantan* (Absolute Millivolts Centigrade Scale)	*Temp. C. or F.*	*Iron vs. Constantan* (Absolute Millivolts Fahrenheit Scale)	*Chromel vs. Alumel* (Absolute Millivolts Fahrenheit Scale)	*Platinum vs. Plat. + 10% Rhodium* (Absolute Millivolts Fahrenheit Scale)	*Copper vs. Constantan* (Absolute Millivolts Fahrenheit Scale)
				–300	–7.52	–5.51		–5.2
				–250	–6.71	–4.96		–4.7
		–5.75		–200	–5.76	–4.29		–4.1
–4.60		–4.81	–6.50	–150	–4.68	–3.52		–3.3
–3.35		–3.49	–4.63	–100	–3.49	–2.65		–2.5
–1.80		–1.86	–2.43	–50	–2.22	–1.70		–1.6
0	0	0	0	0	–0.89	–0.68		–0.6
2.035	0.299	2.02	2.58	50	+0.50	+0.40	0.056	0.3
4.277	0.643	4.10	5.27	100	1.94	1.52	0.221	1.5
6.703	1.025	6.13	8.00	150	3.41	2.66	0.401	2.7
9.288	1.436	8.13	10.78	200	4.91	3.82	0.595	3.9
12.015	1.868	10.16	13.56	250	6.42	4.97	0.800	5.2
14.864	2.316	12.21	16.33	300	7.94	6.09	1.017	6.6
17.821	2.778	14.29	19.09	350	9.48	7.20	1.242	8.0
20.874	3.251	16.40	21.85	400	11.03	8.31	1.474	9.5
	3.732	18.51	24.61	450	12.57	9.43	1.712	11.
	4.221	20.65	27.39	500	14.12	10.57	1.956	12.
	4.718	22.78	30.22	550	15.65	11.71	2.205	14.
	5.224	24.91	33.11	600	17.18	12.86	2.458	15.
	5.738	27.03	36.08	650	18.72	14.02	2.716	17.
	6.260	29.14	39.15	700	20.26	15.18	2.977	19.
	6.790	31.23	42.32	750	21.79	16.35	3.240	20.
	7.329	33.30	45.53	800	23.32	17.53	3.506	
	7.876	35.34	48.73	850	24.85	18.70	3.775	
	8.432	37.36		900	26.40	19.89	4.046	
	8.997	39.35		950	27.95	21.07	4.319	
	9.570	41.31		1000	29.52	22.26	4.596	
	10.152	43.25		1050	31.12	23.44	4.874	
	10.741	45.16		1100	32.72	24.63	5.156	

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Electromotive Force vs. Temperature

Thermocouples

Platinum vs. Plat. + 10% Rhodium (Degrees Centigrade)	Chromel vs. Alumel (Degrees Centigrade)	Iron vs. Constantan (Degrees Centigrade)	EMF in Absolute mv.	Iron vs. Constantan (Degrees Fahrenheit)	Chromel vs. Alumel (Degrees Fahrenheit)	Platinum vs. Plat. + 10% Rhodium (Degrees Fahrenheit)	Copper vs. Constantan (Degrees Fahrenheit)
	555	421	23	790	1031		
	579	439	24	822	1074		
	602	457	25	855	1116		
	626	475	26	887	1158		
	649	493	27	919	1201		
	673	511	28	952	1243		
	697	529	29	983	1286		
	721	546	30	1015	1329		
	744	564	31	1046	1372		
	768	581	32	1078	1415		
	793	598	33	1108	1459		
	817	615	34	1139	1503		
	842	632	35	1170	1547		
	866	649	36	1200	1591		
	891	665	37	1229	1636		
	916	681	38	1259	1681		
	941	698	39	1288	1726		
	967	713	40	1316	1772		
	992	729	41	1345	1818		
	1018	745	42	1373	1864		
	1044	761	43	1401	1911		
	1069	776	44	1429	1957		
	1096	792	45	1457	2004		
	1122	807	46	1485	2052		
	1149	823	47	1513	2100		
	1176	839	48	1541	2149		
	1203	854	49	1570	2197		
	1231	870	50	1599	2247		
	1258		51		2297		
	1287		52		2348		
	1315		53		2400		
	1344		54		2452		
			55		2505		
			56				
			57				
			58				
			59				
			60				
			61				
			62				
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Temperature vs. Electromotive Force

Thermocouples

Copper vs. Constantan (Absolute Millivolts, Centigrade Scale)	Platinum vs. Plat. + 10% Rhodium (Absolute Millivolts, Centigrade Scale)	Chromel vs. Alumel (Absolute Millivolts, Centigrade Scale)	Iron vs. Constantan (Absolute Millivolts, Centigrade Scale)	Temp. C. or F.	Iron vs. Constantan (Absolute Millivolts, Fahrenheit Scale)	Chromel vs. Alumel (Absolute Millivolts, Fahrenheit Scale)	Platinum vs. Plat. + 10% Rhodium (Absolute Millivolts, Fahrenheit Scale)	Copper vs. Constantan (Absolute Millivolts, Fahrenheit Scale)
	11.336	47.04		1150	34.36	25.81	5.440	
	11.935	48.89		1200	36.01	26.98	5.726	
	12.536	50.69		1250	37.71	28.15	6.015	
	13.138	52.46		1300	39.43	29.32	6.307	
	13.738	54.20		1350	41.19	30.49	6.601	
	14.337			1400	42.96	31.65	6.897	
	14.935			1450	44.75	32.80	7.196	
	15.530			1500	46.53	33.93	7.498	
	16.124			1550	48.31	35.07	7.803	
	16.716			1600	50.05	36.19	8.110	
	17.305			1650		37.31	8.420	
	17.891			1700		38.43	8.732	
	18.474			1750		39.53	9.048	
				1800		40.62	9.365	
				1850		41.70	9.686	
				1900		42.78	10.009	
				1950		43.85	10.334	
				2000		44.91	10.662	
				2050		45.96	10.992	
				2100		47.00	11.323	
				2150		48.03	11.655	
				2200		49.05	11.989	
				2250		50.06	12.322	
				2300		51.05	12.657	
				2350		52.03	12.991	
				2400		53.01	13.325	
				2450		53.97	13.658	
				2500		54.92	13.991	
				2550			14.324	
				2600			14.656	
				2650			14.988	
				2700			15.319	
				2750			15.649	
				2800			15.979	
				2850			16.308	
				2900			16.637	
				2950			16.965	
				3000			17.292	
				3050			17.618	
				3100			17.943	
				3150			18.267	
				3200			18.590	

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